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PHYSICAL MEMOIRS,

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PHYSICAL MEMOIRS.

STUDIES
ON
ELECTRIC BOUNDARY-LAYERS.

BY

PROFESSOR H. VON HELMHOLTZ.

Studien über elektrische Grenzschichten. Wiedemann's Annalen, Bd. vii. p. 337, 1879; also 'Wissenschaftliche Abhandlungen von H. Helmholtz,' vol. i. pp. 855–898.

THE theory hitherto held of the distribution of electricity among a system of conductors takes account only of the forces exerted by this agent as known from its effects at a distance, and it arrives at the following conclusion: that electricity existing in equilibrium upon one or more conducting bodies leaves the interior of the bodies entirely free, and merely forms an infinitely thin layer on their surfaces. That this layer is actually very thin, and that only vanishingly small quantities of electricity are retained within the mass of a conductor, are made evident by all the experiments in which an electrified conductor is allowed to discharge itself onto an entirely separate and insulated conducting envelope, and its electrical condition investigated after removal of the envelope.

So long as we have to do only with a simple electric boundary-layer or a conductor in contact with surrounding conductors or insulators, without any discontinuity in the value of the potential function, the hypothesis of a finite

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quantity of electricity spread out in an infinitely thin layer, the volume-density of which must therefore be reckoned infinite, presents no difficulty, since the work-equivalent of any one portion of such an accumulation of electricity, which is equal to half the product of the quantity of electricity considered and the value of the potential function * obtaining at the position where such portion is situated, remains finite.

It is quite otherwise, however, with those cases in which a discontinuity exists in the value of the potential function at the separating surface of two different bodies ; and among these cases the one best known and most investigated is that of two conductors in contact under the influence of galvanic force acting between them. In order that a difference in the value of the potential function should be manifested, an "electric double layer" must in this case be set up along the bounding surface.

If two plates, one of pure zinc and one of copper in metallic connexion with it, be placed with their surfaces near together, a quantity of positive electricity accumulates on the zinc plate, and of negative on the copper plate, which continually increases as the plates are brought nearer together. If we designate the distance apart of the plates by D, and the density of positive electricity on the zinc plate, which is equal to that of negative on the copper plate, by e, the product eD remains constant however closely the plates approach each other. I have called this product the "moment of the electric double layer"†. This is equal to the difference between the values of the potential function for the two plates divided by 4π. Since, then, this difference of potential remains of constant magnitude, even if the plates come into the same perfect contact as there is at the already existing point of connexion, the moment of the electric double layer set up along their boundary-surface must even in this case remain unchanged.

Sir W. Thomson has already called attention to the fact that the formation of this electric double layer represents an expenditure of work the amount of which per unit of surface

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* [Here and afterwards Prof. Helmholtz uses "potential function" for what is usually called "potential" by English writers.]

† Pogg. *Ann.* lxxxix. p. 211, 1853. *Wissen. Abh.* pp. 489–491.

is in electrostatic measure (the difference of potential being $P-P_1$):—

$$\tfrac{1}{2}(P-P_1)e=2\pi D\,.\,e^2=\frac{(P-P_1)^2}{8\pi D}$$

The corresponding amount of work may be done either mechanically, through the attractive force which the metallically connected and thereby charged plates exert on one another during their approximation, or thermally, if the plates be brought near together on insulated stands and then put in connexion by means of a conducting wire so as to allow them to become charged electrically for the first time. The movement of electricity thus set up would give rise to heat in the connecting wire, in accordance with the law demonstrated by Riess for Leyden batteries. This work-expenditure, as its value given by the above expression shows, would be infinite when $D=0$, and e accordingly infinite. Sir W. Thomson asserts that this expenditure of work for the greatest extension of surface of two given metals is at most the equivalent of the heat developed in melting them together, since in this case their combination is certainly more complete than that due to the mere laying upon one another of leaves of metal prepared from them. If these leaves could be made so thin as just to receive the electric double layer, the limit of their electric expenditure of work would be reached. In this way a minimum value of D may be discovered. Sir W. Thomson estimates this as the thirty-millionth of a millimetre*.

A case of actual molecular contact of two conductors, with the possibility of a changeable discontinuity of potential, is afforded us by metallic electrodes in an electrolyte which cannot be decomposed by the electromotive forces employed. In this case also an electric double layer, the electric moment of which corresponds to the sudden change of potential, existing at the time, from the electrode concerned to the fluid, must be set up at the surface of the electrodes under the influence of the polarizing current, and be capable of discharging itself in the depolarizing current, so far as it is not dissipated by diffusion or residual metallic conduction in the electrolyte.

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* Silliman's Journ. (2) L. pp. 38–44, 258–261, 1870. Nature, Mar. 31 and May 19, 1870.

Kohlrausch's investigations on the electrolytic capacity of a platinum surface, in the case of the electrolysis of water, give for the mean distance of such layers the 2,475,000th part of a millimetre, if we suppose the polarization shared equally by the two plates, or double this if the whole action takes place at the plate charged with hydrogen. If, moreover, the oxygen and hydrogen are in this case carried along with the electricity, the potential-difference, as it shows itself on the distant parts of a conductor, depends only on the accumulation of the electricities combined with the atoms of the two elements.

The force which does work in forming the galvanic charge on two metals in contact can only be sought in a different attraction of different metals for the two electricities, as I have already explained in my treatise on the Conservation of Force*. Let us denote by K_c the quantity of potential energy represented by the attraction of copper for a positive unit of electricity when this is at a distance great compared with the molecular forces, a quantity which is accordingly lost when this unit of electricity passes to the interior of the copper; let us denote by K_z the same number for zinc; then the gain of potential energy due to the passage of the quantity of electricity dE from the copper at potential P_c to the zinc at potential P_z is

$$dE(K_c - K_z - P_c + P_z).$$

In the state of equilibrium this work must equal zero, or

$$P_c - K_c = P_z - K_z;$$

or the two metals in conducting contact would attain the constant difference of potential,

$$P_z - P_c = K_z - K_c.$$

Let us add another metal, platinum, with suffix p; then

$$P_p - P_c = K_p - K_c$$

$$P_p - P_z = K_p - K_z = (K_p - K_c) + (K_c - K_z).$$

These equations contain the law of the electromotive series, which therefore follows immediately from this hypothesis. This law holds for bodies which conduct without electrolysis and are at the same temperature. In such the electricity tends to condition of equilibrium. That it cannot attain such a condition when an electrolytic conductor is interposed, but remains as a continuous current, may be referred, in the sense of the theory here given, to the fact that the latter class of conductors falls under the fixed conditions of continuous chemical transformation, and the attainment of statical equilibrium is thereby prevented.

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* [Taylor's 'Scientific Memoirs,' new series (Nat. Phil.), p. 114.]

Each of the above quantities K is the work done by a force which comes into action only at molecular distances. We may therefore suppose that the quantity K_z does not increase suddenly to the value K_c in passing through the common surface of the two metals, but continuously within a boundary-layer the breadth of which is of the same order of magnitude as the sphere of action of the molecular forces. Accordingly the quantities

$$P-K=P_c-K_c=P_z-K_z$$

in the electric boundary-layer may maintain a constant value, so long as no other forces act simultaneously upon them, and the density of electricity at a small distance x from the bounding surface would be given by the equation

$$-4\pi\epsilon=\frac{\partial^2 P}{\partial x^2}=+\frac{\partial^2 K}{\partial x^2}.$$

This gives also a finite value to the electric density, and thence also a finite value to the quantity of electric work. Other electric forces may also possibly have an influence arising from the combination of equivalents of electricity with the ponderable atoms, as is shown in the case of electrolysis. Such forces have been investigated by B. Riemann* in his "Theory of the residual charge of electric condensers" (*Theorie des Rückstandes elektrischer Bindungsapparate*).

There is no reason to limit the existence of the force denoted by K to good conductors, and in fact the phenomena of frictional electricity, treated from this point of view, connect themselves quite naturally with those of galvanic charges.

If two metals be separated from each other, then that amount of charge remains on them which existed at the moment of last contact at a single point of the surface, since the electricity puts itself in equilibrium with a rapidity compared with which that of the mechanical motion vanishes. This remaining charge is moreover of very inconstant magnitude, since the position of the plates at the moment at which the last contact occurred would always show small differences which might have a very great influence on the density of the electric charges still existing upon them. If, however, one or both bodies be insulated only very incomplete discharge can occur, and the electricities bound on what was previously the common separating surface would then become separate and free. A simple calculation shows that in this way they may attain to very high values of the potential.

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* *Gesammelte Werke*, p. 345. Leipzig, 1876.

Let us suppose that circular copper and zinc plates of radius R, the electromotive force between which we will put equal to A, have formed a double layer of thickness D, and can be separated without discharging; then for electromotive force A and distance D

$$+4\pi\epsilon=\frac{A}{D},$$

and the quantity of electricity accumulated on each disk is

$$\pi R^2\epsilon=\frac{AR^2}{4D}.$$

The density of this amount distributed over each of the conducting disks after they are separated from each other would be

$$e=\tfrac{1}{2}\frac{R\epsilon}{\sqrt{R^2-\rho^2}},$$

and the potential

$$P=\tfrac{1}{2}\pi^2R\epsilon=\tfrac{1}{8}\pi\frac{RA}{D}.$$

If we put $R=10$ cm. and D equal to the millionth of a millimetre, the difference of potential between a plate of either metal and a plate of the other metal put to earth would be increased 39,270,000 times.

Since according to Sir W. Thomson's* measurements a battery of 5510 Daniells is in a condition to transmit a spark $\frac{1}{8}$ cm. long between very slightly curved plates, these plates would, if A be put equal to the force of one Daniell, transmit sparks 891 cm. long, if the proportionality of striking distance to difference of potential reach to such distances.

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* Papers on Electrostatics, p. 259.

These calculations enable us to perceive that, with perfect insulation, electromotive forces, even if much smaller than the galvanic tension between copper and zinc, can give rise to such actions as are exhibited by our electrical machines; and on the other hand that success in obtaining powerful actions of the latter kind depends essentially on the complete absence of conductivity on the part of at least one of the rubbed bodies, which is in full agreement with practical experience.

Friction under moderate pressure may accordingly be considered as the means of obtaining a very complete and widely extended contact of two electrically different bodies, and at the same time getting rid of all layers of foreign material attached to their surface. However, the potential series for frictional electricity is very incompletely determined, and the mutual relations of different substances change under modifications which are obviously very minute or even altogether unrecognizable. This is explained in part by the fact that only the most superficial layer, perhaps the millionth of a millimetre thick, takes part in the action. This may be changed without our recognizing it; it may be detached by friction, and an electric charge may make its appearance developed between it and the substance within. Or it may be that other charges have left behind their residua on the insulator, and that these have become inactive externally by reason of the opposite charging of the surface. If the surface-charge be torn off by friction, it may be that this earlier electrification may then become apparent. In this way very many of the irregularities which arise in the friction of bodies standing near together in the potential series may be explained.

So long as the two rubbed bodies lie close together, the corresponding electric double layers are held fast by the attraction of the ponderable molecules, and their potential function has a minimum value, since the two opposite layers are close together. If they be separated their potential rapidly rises, and since sparks can pass between a strongly-charged insulator and a conductor, these sparks being obviously connected with the transport of separated and electrified ponderable particles, there is a risk lest immediately behind the line of separation of the two surfaces a partial combination of the dissociated electricities should take place, if one of the two have conducting power sufficient to allow of the rapid flow of electricity needed for the spark-discharge.

This risk is obviated in the ordinary construction of the electrical machine, by attaching to the hinder edge of the cushion a piece of insulating tissue which stands to the disk in the same electric relation as the amalgamed metallic surface. Under these conditions, the electric double layer remains bound in consequence of the molecular forces up to the margin of the varnished silk, at which point no sensible spark-discharge between the two insulators glass and silk can occur.

The forward end of the cushion must, however, be well connected to earth, in order that it may give off positive electricity to the approaching parts of the disk which have been discharged against the prime conductor, or, otherwise, that the negative electricity may be conducted away. The combination of a system, conducting only at the beginning and insulating at the end, to form the cushion answers in this connexion both requirements.

In order to observe in the simplest way the springing back of the charge across the line of separation of the bodies rubbed, it is only necessary to watch an electrical machine in the dark, either after taking off the silken appendage to the cushion, or while turning the machine backwards. If the space between the edge of the cushion and the issuing disk be examined a persistent ring of brushes may be seen, which partially discharge the portions of the disk just becoming free against the cushion. If, however, the machine be turned in the usual direction and the layers of silk disposed along the disk, nothing can be seen of any luminous appearance at their free edges.

How large a part of the electricity of the disk is discharged backwards if the hinder end of the cushion be unprotected is shown if we allow the electricity from the machine to flow into a unit-jar, and observe the number of turns intervening between two discharges of the jar. In an experiment of this kind I set the arm of the conductor of a machine with two cushions midway between the edge of the silk and that of the next cushion, so that the distance from the rubbed part of the disk through the air to the conductor was equally great both in forward and backward rotation. It turned out that the disk gave up twice as much electricity to the conductor in the first case, in which protection was afforded by the silk, as in the latter case, although in the first the path from the rubbed surface of the glass which it traversed under the silk was longer by about a quadrant. Thence it followed that when the unprotected disk left the conducting part of the cushion, about half the accumulated electricity discharged itself backwards upon the cushion.

The luminous appearance observed in a barometer in the dark, when the top of the mercury moves downwards *in vacuo*, is of the same kind.

Accordingly when a semi-conductor, such as leather, slides over a glass surface, in which case the glass takes a positive and the leather a negative charge, the positive electricity of the glass must strike back in part to the leather across the line of separation, while the half-discharged glass on reaching the forward edge of a fresh leather surface again withdraws positive electricity from the leather and gives up negative to it. Thence the so-called "frictional currents," described by Zöllner*, are very simply explained. These are naturally greatly intensified if good metallic conductors be attached to the ends of the cushion, such as the galvanometer wires and the pieces of tinfoil† which in Zöllner's experiments were placed round the ends of the cushions. If all loss of electricity from the rubbed glass could be avoided from the moment at which it leaves the hinder edge of the cushion to that at which it is brought to it again, these supposed frictional currents would disappear. Since, however,—in addition to the discharge from the strongly electrified disk against the cushion,—the air, the dust suspended in it, the imperfect insulation of the glass, and brush discharges against conductors at a considerable distance, may all produce loss, it follows that a

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[*] Pogg. *Ann.* clviii. pp. 479–539, 1876. I mention the fact here as it appears that some physicists have not remarked the bearing of this phenomenon.

[†] *L. c.* Taf. vi. fig. 4, *s*.

slight difference of electric potential between the front and back edges of the cushion always exists.

That even the best insulators possess a slight conductivity is shown by the residual charge of the Leyden jar; and by Wüllner's investigation, according to which, by continued action of electric forces, a state of electric distribution is finally attained in all insulating bodies which answers to the condition of electric equilibrium. Hence it is possible that even with insulators the electric charge of their boundary-layers in contact is set up through mutual exchange of the opposite electricities, as in the case of metals. Since the spaces across which the electricity would have to be thus driven only attain to millionths of a millimetre, and within this short space a finite fall of potential, *i. e.* an extraordinarily great electromotive force, acts, considerable quantities of electricity must obviously be transferred in a very short time, even if the attainment of complete equilibrium demand many hours, as, for example, is the case in the residual phenomena of the Leyden jar. That, moreover, in the ordinary electrical machine the time of passage through the cushion is insufficient for the complete charging of the disk, is shown by the fact that with slower rotation fewer turns are needed for the charging of a unit jar than with more rapid, supposing the insulation be good.

A peculiar intermediate case, affording a transition between the electrical excitation due to the galvanic opposition of substances at rest and that set up by the sliding friction of solid bodies, occurs in the phenomena presented by the flow of liquids past a solid wall which they wet. Although here the outermost layer of liquid probably in most cases clings immovably to the wetted wall (further evidence for which we shall find in what follows), and therefore, properly speaking, fluid is displaced only against fluid in the neighbourhood of the wall; yet we find that ponderomotive and electromotive forces are set up which are due to contact with the wall. This has been demonstrated in my opinion in a very satisfactory manner by Prof. Quincke, both as regards the transfer of liquid under the action of electric currents, and as regards the electromotive forces set up by the motion of the liquid. A valuable supplement to his proof is given by the recently published work of J. Elster*. This class of phenomena is distinguished by the fact that a number of known quantitatively defined laws of the phenomena have been demonstrated by Profs. G. Wiedemann and Quincke. The kind of fluid motion which here offers itself is—at least in those cases in which, by the use of sufficiently narrow tubes and moderate velocities, the effects of fluid friction have time to become fully established and to bring about a stationary condition—well known, theoretically deducible, and has been compared with the actual phenomena, by Poiseuille's method, by a succession of observers.

I have endeavoured in what follows to show that the laws of these phenomena found by experiment may be entirely deduced from the hypothesis here laid down regarding the nature of galvanic difference of tension, at least in those cases in which the liquid obeys the conditions of flow which lie at the foundation of Poiseuille's laws.

The assumptions in my explanations are therefore the following:—The liquid stands in galvanic opposition to the walls of the tube, and the two build up an electric double layer along their bounding surface. The portion of this layer falling within the fluid is in general—omitting the exceptions pointed out by G. Quincke—positive. It is of extremely small, though not of vanishing thickness. The side of this layer turned towards the bounding surface, at least in those cases in which the experimentally found laws hold, clings immovably to the wall; the remainder can be displaced, subject, however, to the internal friction of the liquid. If an electric current be led through the liquid, producing a fall of potential, and therefore ponderomotive electric forces able to act on the electrically-charged parts, these forces drive along the positively-charged wall-layer of liquid. It results, however, from the internal friction of the liquid that the whole cross section of the tube takes up the same state of motion, if no hydraulic back-pressure prevent it. If there be any such, the motion of the liquid due to the pressure adds itself on to that produced by the forces of electric attractions. If the pressure drives just as much liquid backwards through any cross section as the electric force drives forwards, a stationary condition of the liquid is set up, in which the flow along the walls of the tube takes place in the direction of the electric force, but in the centre in that of the hydrostatic pressure.

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* Wied. *Ann.* vi. p. 553, 1879.

If, on the other hand, no external electromotive force acts on the tube, but a hydrostatic pressure which propels primarily the water, then also the inner parts of the electrically charged boundary-layer of the liquid will be carried along at the same time. So long as this is displaced parallel to the wall of the tube with uniform velocity, and therefore remains continuously under the influence of the galvanic forces, its electrical equilibrium is not disturbed. Outside the exit end of the tube, however, it is either torn away from the wall by vortex motion, or, if it remain thereon, is forced into a thicker layer by the diminished stream-velocity. By both processes its positive charge is liberated from the restraining influence of the negative layer on the wall, and becomes free.

Conversely, at the beginning of the tube fresh layers are approaching the wall, and since the latter already possesses a negative charge, the approaching liquid must withdraw from the rest its positive electricity and leave negative therein.

The negative electricity accumulated before the entrance of the tube and the positive electricity collected beyond the end compensate each other again, partly through the liquid column in the tube, partly through any other conducting path offered them. In such a conductor, therefore, a galvanic current will show itself. If there be no other conducting path, the difference o felectric potentials between the ends of the tube must increase until as much electricity flows back by conduction along the tube as is driven forward with the water-particles by convection.

In its essential outlines this explanation agrees with that given by G. Quincke*. He was at that time able to determine the movements of the rubbing fluid, but not to follow them out in detail so thoroughly as is possible with the help of our present knowledge, and, accordingly, he was able to deduce quantitative determinations from his theoretical treatment only for a few of the simplest conditions.

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* Pogg. *Ann.* cxiii. pp. 513–598, 1861.

Sufficient experimental data exist to allow of our calculating the magnitude of the galvanic tension between liquid and wall which must be assumed according to the theory just sketched. It appears that this does not differ to any very considerable degree from the observed values of the galvanic force between metals, and that it may be put equal to the electromotive force of a Daniell's element, or of a small number of such elements.

§ 1. *Fluid transported by an Electric Current.*

Let us conceive of a conducting liquid enclosed in an insulating cylindrical tube, with an electric double layer at the boundary of the two, the thickness of which we may consider vanishingly small compared with the linear dimensions of the cross section of the tube. Let the axis of the tube be the axis of x, the velocity of the fluid parallel to it u, but the velocity-components perpendicular to the axis of the tube everywhere equal to zero; then, according to the hydrostatic laws for an incompressible fluid, we must have

$$\frac{\partial u}{\partial x}=0,$$

that is, u must be a function of y and z only. I note that the manner of flow here assumed in sufficiently long tubes does not necessarily exist from the beginning of the tube, but arises in its further portions under the influence of friction and then persists up to the end of the tube. This is the type of motion for which Poiseuille's law holds.

Let us further denote the hydrostatic pressure by p, the coefficient of friction of the liquid by k^2, and the electric force parallel to the x-axis acting on unit volume of the liquid by X, then the equation of flow for the stationary current is

$$\mathrm{X}-\frac{\partial p}{\partial x}=-k^2\left(\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\right) \quad . \quad . \quad . \quad . \quad (1)$$

Let ϵ be the electric density on the external layer of liquid, which likewise is a function of y and z only, not of x; moreover let J be the current-strength, σ the specific resistance of the liquid, ϕ the electric-potential function—all these quantities being measured in electrostatic measure—and Q the cross section of the tube; then, according to Ohm's law,

$$-\frac{\partial\phi}{\partial x}=\frac{J\sigma}{Q},$$

and

$$X=-\epsilon.\frac{\partial\phi}{\partial x}=\epsilon.\frac{J\sigma}{Q}. \quad . \quad . \quad . \quad . \quad (1\,a)$$

Equations (1) and (1 *a*) combine into

$$-\epsilon.\frac{J\sigma}{Q}+\frac{\partial p}{\partial x}=k^2\left(\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\right). \quad . \quad . \quad (1\,b)$$

Since u and ϵ must be independent of x, the same must consequently hold for $\frac{\partial p}{\partial x}$. This may therefore be put constant :

$$\frac{\partial p}{\partial x}=\frac{P}{L},$$

where P is the difference of pressure between the ends of the tube, and L its length.

The boundary condition for the fluid moved against the wall of the tube when this is in a condition to slide along this wall is, if l denote the coefficient of slip for the rubbing fluid and N the normal drawn inwards,

$$\bar{u}=l\frac{\partial u}{\partial N}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1\,c)$$

In order to satisfy equations (1 *b*) and (1 *c*) we can divide the function u into two parts,

$$u=u_0+u_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

so that

$$\frac{P}{L}=k^2\left(\frac{\partial^2 u_0}{\partial y^2}+\frac{\partial^2 u_0}{\partial z^2}\right), \quad . \quad . \quad . \quad . \quad (2\,a)$$

$$-\frac{\epsilon\sigma J}{Q}=k^2\left(\frac{\partial^2 u_1}{\partial y^2}+\frac{\partial^2 u_1}{\partial z^2}\right), \quad . \quad . \quad . \quad . \quad (2\,b)$$

$$\bar{u}_0=l\frac{\partial u_0}{\partial N}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2\,c)$$

$$\bar{u}_1=l\frac{\partial u_1}{\partial N}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2\,d)$$

This supposition satisfies the condition prescribed by the differential equations. The motion u_0 is that which arises in the rubbing fluid under the influence of hydrostatic pressure; u_1, on the other hand, is that which would be set up by the electric force in the absence of hydrostatic pressure; the two are simply superposed.

Let us compare with equation (2 b) the equation derived from the laws of electric potential-functions; remembering that

$$\frac{\partial^2\phi}{\partial x^2}=0,$$

we have

$$-4\pi\epsilon=\frac{\partial^2\phi}{\partial y^2}+\frac{\partial^2\phi}{\partial z^2},$$

whence we obtain

$$0=\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\left(\phi-\frac{4\pi k^2 Q}{J\,.\,\sigma}\,.\,u_1\right);$$

whence it follows, since, if J be constant, ϕ is a linear quantity depending on x but u_1 is not, that

$$\phi-\frac{4\pi k^2 Q}{J\sigma}u_1=C-\frac{\sigma J x}{Q}+by+cz\,;\text{*}$$

where C, b, c are constants of integration.

Equation (2 c) accordingly gives at the boundary

$$\phi_a-l\frac{\partial\phi}{\partial N}=C-\frac{\sigma J x}{Q}+(\bar{b}y+\bar{c}z)-l\left(b\frac{\partial y}{\partial N}+c\frac{\partial z}{\partial N}\right).$$

Since ϕ is the potential function of the double layer uniformly distributed round the tube it must, provided that the thickness of this layer as compared with the radius of curvature of the surface everywhere vanishes, have the same value at all parts of the circumference, and the members of the last equation depending on y and z must vanish, that is, $b=c=0$. In the middle of the tube, where $\epsilon=0$, we can therefore put

$$\phi_i=-\frac{\sigma J x}{Q};$$

and obtain therefore

$$\phi_a-\phi-l\frac{\partial\phi}{\partial N}=C.$$

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* A misprint in the factor of x is here corrected. 1881. [In Wied. *Ann.* the coefficient of x is turned upside down; in *Wissensch. Abh.* this is corrected, but x is omitted: both errors are here corrected.—E. F. J. L.]

Accordingly the value of the flow will be

$$\frac{4\pi k^2 Q}{J\sigma} \cdot u_1 = \phi_i - \phi_a + l\frac{\partial \phi}{\partial N}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If no difference of hydrostatic pressure exist between the two ends of the tube, the other component of current u_0 will be equal to zero, and u_1 is the only component present. The whole amount of liquid U_1 flowing through each section of the tube depends therefore only upon u_1. According to the hypothesis laid down, whenever the thickness of the electric layer, within which smaller values of u_1 exist, vanishes in comparison with the dimensions of the cross section Q of the tube, we can treat the value of u_1, which is constant at the middle of the tube, as constant for the whole section, and therefore obtain

$$U_1 = \frac{\sigma J}{4\pi k^2} \cdot \left(\phi_i - \phi_a + l\frac{\partial \phi}{\partial N}\right), \quad . \quad . \quad . \quad (3\,a)$$

which value is independent of the dimensions of the tube.

Let us further denote by A the electromotive force which maintains the current J in length L of the tube ; then

$$\frac{J\sigma L}{Q} = A\,;$$

we can therefore put the value of the discharge into the form

$$U_1 = \frac{QA}{4\pi L k^2} \cdot \left(\phi_i - \phi_a + l\frac{\partial \phi}{\partial N}\right), \quad . \quad . \quad . \quad . \quad (3\,b)$$

a value which is independent of the specific resistance of the liquid.

We may treat plates of porous clay as walls which are pierced by a system of fine pores. A determination of the weight of water imbibed by one of the cells ordinarily employed for galvanic batteries, and of the specific gravity of the moist cell, showed that the solid clay occupies about twice as much space as the canal-pores which it leaves. If we then suppose that canal-pores of circular section penetrate uniformly through the clay in all directions, the permeability for diffusion of pressure, which is made clear by a number of investigations of G. Wiedemann and G. Quincke relating to the clay partitions employed by them, proves that the mean diameter of these canals must be reckoned at from $\frac{1}{13}$ to $\frac{1}{40}$ mm.; so that it would be, in accordance with this, still very great compared with the probable thickness of the electric boundary-layer. The assumption made in our calculations with reference to this point may therefore be looked upon as fulfilled in the case of experiments with clay plates. Since it bears only on the latter point, I omit here the carrying out of special calculations. Further, I know of no cases in which all the data necessary for the calculation have been obtained with one and the same clay plate of regular shape.

The number of tubes increases in proportion to the area, their length in proportion to the thickness of the flat plate employed. If the clay plate and the liquid remain uniform, the quantity of liquid transmitted, in the absence of hydrostatic pressure, must therefore, in accordance with equation (3 *b*), be proportional to the difference of potential between the two sides of the plate and to its area, and inversely proportional to its thickness, as G. Wiedemann discovered [*]. Aqueous fluids flow through the clay plate in the direction of the positive electricity, and they must therefore have acquired a positive tension as compared to the clay wall. On the other hand, if the intensity of the current be uniform, neither the thickness L of the plate nor its area have any influence, as equation (3 *a*) shows, for in every single tube the intensity varies in an inverse ratio to the number of tubes N, and therefore the product NJ remains constant; this is likewise in agreement with G. Wiedemann's investigations. He has given in § 5 of his second paper, "*Ueber die Bewegung der Flüssigkeiten im Kreise der geschlossenen galvanischen Säule*"[†], a series of measurements from which the difference of potential $(\phi_i - \phi_a)$ may be calculated, on the assumption that no slipping exists. For the rest we shall see later, in discussing Quincke's investigations, that there are definite facts which are opposed to the existence of slipping in cases of this kind.

In the researches mentioned, the quantity of copper separated by the current was determined voltametrically. Now, according to R. Bunsen, Weber's electromagnetic unit of current decomposes 0·0092705 mgr. of water per second. Since the equivalent, Cu, of copper bears to that of water the ratio of 63·3 : 18, and since, according to the younger Kohlrausch, a Daniell's cell has an electromotive force, D, of 11·71 Weber-Siemens units, a Daniell's cell in a circuit whose resistance is one Siemens unit, S, gives 0·38176 mgr. of copper per second, a quantity we denote by γ. If, therefore, the quantity of copper deposited by a current lasting for t seconds be g mgr., then

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[*] Pogg. *Ann.* lxxxvii. pp. 321–352, 1852.

[†] Ibid. xcix. p. 199, 1856.

$$\mathrm{J}t = \frac{g \,.\, \mathrm{D}}{\gamma \,.\, \mathrm{S}},$$

where D denotes the electromotive force of a Daniell's element.

Therefore, according to equation (3 a),

$$\frac{\gamma \,.\, \mathrm{U}t \,.\, \mathrm{S}}{g \,.\, \mathrm{D}} = \frac{\sigma}{4\pi k^2}(\phi_i - \phi_a).$$

G. Wiedemann has expressed σ in units which correspond to the resistance of platinum, *i. e.* which are equal to the resistance of a cube of platinum 1 mm. in the edge. The resistance of a millim. cube of mercury is 0·001 of a Siemens unit; the conductivity of platinum bears to that of mercury, according to Matthiessen, the ratio of 10·53 : 1·63 = 6·46 : 1. Thence the resistance of the platinum cube is S/m, if we put

$$m = 6460 \text{ mm.}^{-1}$$

If σ'* denote Wiedemann's number, then, instead of the quantity σ*, we must put

$$\sigma' \,.\, \frac{\mathrm{S}}{m}.$$

The quantity k_0^2 for water at 15° is, according to Poiseuille, equal to 1·1441 mgr. mm.$^{-1}$ sec.$^{-1}$†. Wiedemann has given the ratio of the time of flow, τ, to that for an equal quantity of water. Then $k^2 = k_0^2 \,.\, \tau$. Our equation therefore becomes, after these substitutions,

$$\frac{\phi_i - \phi_a}{\mathrm{D}} = \frac{4\pi k_0^2 \gamma m}{\mathrm{D}^2} \,.\, \frac{\mathrm{U}t}{g} \,.\, \frac{\tau}{\sigma'}.$$

The left side of the equation gives the value of the required difference of potential expressed as a fraction of that produced by a Daniell's element. The quantity D^2 on the right-hand side is to be measured in electrostatic units, in which its value is given by

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* [These σ's are misprinted as b's in the original.—E. F. J. L.]

† This should be, in accordance with the notation of the work carried out by myself and von Piotrowski (*Wien. Sitzungsber.* xl. 1860; *Wissensch. Abh.* pp. 215, 218), denoted by $k_2 h$, where h signifies the density of the fluid. (In the original the number is quoted incorrectly, the last column of the following table is therefore corrected. 1881.)

$$D=0{\cdot}374 \text{ mm.}^{\frac{1}{2}} \text{ mgr.}^{\frac{1}{2}} \text{ sec.}^{-1}$$

The quantity Ut is in our case a volume, which is to be expressed in cubic millimetres.

The data given by G. Wiedemann make it possible to calculate the value of the electric moment, so far as it falls within the liquid, for the four following liquids :—

In 1000 c.c. of solution are contained		Volume of fluid transferred, c.mm.	Quantity of cation deposited, mgr.	Ratio of time of flow to that of equal vol. of water.	Resistance, σ', of the solution, that of Pt being taken as 0·001.	$\phi_i-\phi_a$ in Daniells.
of	mgr.					
Sulphuric Acid. Cu.*						
SO_3	76·56	2800	3770	1·166	179·0	1·2265
	47·36	1510	1174	1·095	289·3	1·2388
Copper Sulphate. Cu.						
$CuSO_4+5H_2O$	149·38	13090	1181	1·417	2247	1·7717
	97·544	12210	904	1·238	3076	1·3781
	89·125	15930	923	1·213	3258	1·6290
Copper Nitrate. Cu.						
$Cu(NO_3)_2$	82·258	3010	1453	1·138	1434	0·4168
	71·852	4360	1903	1·118	1559	0·4165
	64·037	6100	1977	1·103	1695	0·5089
	42·010	2540	550	1·061	2409	0·5157
Silver Nitrate. Ag.						
$AgNO_3$	79·74	5730	2239	1·014	1876	1·1964
	79·46	7600	2765	1·014	1878	1·2832
	29·867	12955	1342	1·003	4656	1·8637

* [*Sic* in original. Query: misprint for H.]

The first three columns of numbers are extracted from Wiedemann's investigation in Pogg. *Ann.* xcix. pp. 192–205, the fourth from those given in the same vol. pp. 222–224, the fifth from those on pp. 227 and 228, and the last two are obtained by interpolating. This is carried out most easily by employing the reciprocal of the resistance, *i. e.* to the conductivity, since the latter is nearly proportional to the contained salt. The last column gives the value I have calculated for the difference of potential between the interior and the boundary of the fluid for the pores of clay partitions. These lie very near together for any single electrolyte, have values which do not exceed the electromotive force of two Daniells, and are generally increased for more dilute solutions. With copper sulphate alone does an increase seem to occur with increased concentration.

§ 2. *Rise of Pressure due to Electric Diffusion.*

The second part of the stream-velocity, which we have denoted above by u_0, and which is maintained by the hydrostatic pressure, we will now determine, subject to the assumption of a circular section for the tube.

The equations

$$\frac{\mathrm{P}}{\mathrm{L}}=k^2\left(\frac{\partial^2 u_0}{\partial y^2}+\frac{\partial^2 u_0}{\partial z^2}\right), \quad \ldots\ldots \quad (2\,a)$$

$$u_0=l\frac{\partial u_0}{\partial \mathrm{N}}, \quad \ldots\ldots\ldots \quad (2\,c)$$

give under these conditions the easily verified value

$$u_0=\frac{\mathrm{P}}{4\mathrm{L}k^2}\cdot(r^2-\mathrm{R}^2)-\frac{l\mathrm{PR}}{2\mathrm{L}k^2}, \quad \ldots\ldots \quad (4)$$

where R denotes the radius of the tube and

$$r^2=y^2+z^2.$$

The fluid volume U_0 flowing through each section is therefore

$$\mathrm{U}_0=2\pi\int_0^{\mathrm{R}} u_0\,.\,rdr=-\frac{\pi\mathrm{PR}^4}{8k^2\mathrm{L}}-\frac{\pi\mathrm{PR}^3 l}{2k^2\mathrm{L}}. \quad \ldots \quad (4\,a)$$

If, through the influence of the current, the pressure be increased so that the water-level remains constant, then we must have

$$U_0+U_1=0,$$

or

$$-\frac{\pi P}{8Lk^2}(R^4+4R^3l)+\frac{R^2A}{4k^2L}\left\{\phi_i-\phi_a+l\frac{\partial\phi}{\partial N}\right\}=0. \quad . \quad (4\,b)$$

Thence it follows, if $l=0$,

$$\frac{\pi}{2}\cdot PR^2=A(\phi_i-\phi_a). \quad . \quad . \quad . \quad . \quad (4\,c)$$

G. Wiedemann has already demonstrated, in his first work on clay partitions, that the fluid-pressure P, to which the liquid can be forced by the electric current, is for similar tube-systems—and, as we must add, for similar tension between the liquid and the wall—proportional to the electromotive force acting between the sides of the partition. Quincke * has demonstrated the same fact for distilled water in capillary glass tubes, through which he led the current of from 40 to 81 Grove's elements. His investigations on cylindrical tubes of varying diameter conducted him to the result that the rise of level is

$$\frac{\Delta h\,.\sin\phi}{22{\cdot}9}=\frac{P}{\epsilon g}=\frac{nb}{R^2}, \quad . \quad . \quad . \quad . \quad (4\,d)$$

in which b for distilled water is equal to 0·000061 millim., n denotes the number of Grove's elements, and R the radius of the tube in millimetres. Δh is the displacement of the water column in scale-divisions, 22·9 of which go to a millimetre, and ϕ the angle of inclination between the tube and the horizon. P is the designation already employed by us for the hydrostatic pressure in absolute measure, ϵ the density of the liquid, and g the intensity of gravity. This result agrees

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* Pogg. *Ann.* cxiii. p. 541 *sqq.*, 1861. On p. 543, l. 7, is a misprint which has passed into several text- and hand-books. It should, in fact, run that "the rise of pressure is nearly *inversely* proportional to the square of the radius of the tube," as Quincke's experimental demonstration and mathematical formula clearly show.

with our equation (4 *c*) obtained subject to the assumption that $l=0$; whence we obtain

$$\phi_i-\phi_a=\frac{\pi\epsilon g b}{2G},$$

where G denotes the magnitude of the electromotive force of a Grove's element in absolute electrostatic measure. If we put the electromotive forces of a Daniell's element equal to 0·374 mm.$^{\frac{1}{2}}$ mgr.$^{\frac{1}{2}}$ sec.$^{-1}$, and that of a Grove 0·6387 of the same unit, we obtain for distilled water against glass

$$\phi_i-\phi_a=3{\cdot}9346 \text{ Daniell.}$$

This value is higher than that found for salt-solutions against clay partitions. But these values also clearly indicate a higher value for pure water.

On the other hand, the investigation must have yielded a different result if the coefficient of slipping, l, had differed from zero. Under otherwise similar conditions the resulting pressures P would have been inversely proportional to the quantity (R^2+4lR). Besides, under these circumstances it is not the difference of potential $(\phi_i-\phi_a)$, but the very much greater quantity $\frac{\partial\phi}{\partial N}$, which is proportional to the density of the layer, that would have determined the result.

Quincke has also made an investigation with tubes the cross section of which was made ring-shaped by means of an enclosed glass fibre. The mean diameter of this fibre was determined, partly by calculation from its weight and length, partly by direct measurement under the microscope with a screw-micrometer. "The values of the diameter determined by the two methods agreed satisfactorily" (*l. c.* p. 529). Since in this case the tubes lay horizontally, we must suppose that the glass fibre lay along the bottom of the tube. The calculation of the quantity of water flowing through under a known pressure can be effected by Kirchhoff's method for determining the partition of electricity upon two neighbouring spheres *, *i. e.* with the help of the electrical images reflected backwards and forwards between two spheres or circles.

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* Crelle's *Journ. für rein. u. angew. Math.* lix. pp. 89–110.

If r be the radius of the tube, the axis of which coincides with the z-axis, and ρ the radius of the cylindrical rod which lies against the side of the tube, so that $r-\rho$ is the distance between the axis of the tube and that of the rod, then the problem is to find a solution of the differential equation

$$4\mathrm{B}=\frac{\mathrm{P}}{\mathrm{L}k^2}=\frac{\partial^2 u_0}{\partial x^2}+\frac{\partial^2 u_0}{\partial y^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

for which, at the surface of the tube

$$x^2+y^2=r^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5\,a)$$

and at the surface of the rod

$$(x-r+\rho)^2+y^2=\rho^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5\,b)$$

the value comes out

$$u=0.$$

Such a solution is

$$u=\mathrm{B}(x^2+y^2-r^2)+2\mathrm{B}r\rho\,.\,\mathrm{V}. \quad . \quad . \quad . \quad (6)$$

The quantity V here denotes the real part of a transcendental function, which latter may be deduced from the function

$$\Psi_\sigma=\underset{k=\infty}{\text{Limit:}}\left\{\sigma\log k-\frac{1}{\sigma+1}-\frac{1}{\sigma+2}\cdots-\frac{1}{\sigma+k}\right\} \quad (6\,a)$$

treated of by Gauss in his memoir on Hypergeometric Series. V is in fact equal to the real part of the difference

$$-\Psi_{\sigma_1}+\Psi_{\sigma_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6\,b)$$

where

$$\sigma_1=\frac{\rho(x+yi)}{(x+yi-r)(r-\rho)}; \qquad \sigma_2=-\frac{r\rho}{(x+yi-r)(r-\rho)}.$$

In forming the integral

$$\mathrm{U}_0=\int u_0\,.\,dxdy,$$

which is to be extended over the space between the two circles, and gives the whole amount of flow, we may avoid integrating over the transcendental V by writing

$$\int \mathrm{V}\, dxdy = \frac{1}{4\mathrm{B}}\int \mathrm{V}\left(\frac{\partial^2 u_0}{dx^2}+\frac{\partial^2 u_0}{\partial y^2}\right)dxdy,$$

and employing the partial integrations made use of in Green's theorem of the potential function, so as to change the integral over the surface into integrals along the circumferences. These are in this case easy to find, if we put

$$u_0=0$$

outside the large circle, and

$$u_0=-2\mathrm{B}(r-\rho)(x-r)$$

inside the small one. The value of u_0 will then be everywhere continuous; at the two circles the leap of its differential coefficient is equal to a constant, and those regions in which the quantity σ is equal to a negative whole number must be separated from the surface of the inner circle by infinitely small enclosing circles, since there the corresponding function Ψ will be infinite. The result is

$$\mathrm{U}_0=-\frac{\pi}{2}\mathrm{B}(r^4-\rho^4)+2\pi\mathrm{B}r^2\rho^2\Psi', \quad . \quad . \quad . \quad (7)$$

where the function

$$\Psi'=\frac{\partial\Psi}{\partial\sigma}$$

is taken for the value

$$\sigma=\frac{\rho}{r-\rho}.$$

Therefore

$$\Psi'=\sum_{n=0}^{n=\infty}\left\{\frac{1}{\left(\frac{\rho}{r-\rho}+n+1\right)^2}\right\}. \quad . \quad . \quad . \quad (7\,a)$$

If this sum be calculated up to a term whose denominator is greater than 4·5 we can find the rest of the series, by calculating, with the aid of five-place logarithms, from the formula applicable with large positive values of σ,

$$\Psi_\sigma' = \frac{1}{\sigma+\frac{1}{2}} - \frac{1}{12}\frac{1}{(\sigma+\frac{1}{2})^3} + \frac{7}{240}\frac{1}{(\sigma+\frac{1}{2})^5} - \ldots, \quad . \quad (7\,b)$$

which may be deduced from the formula given by Gauss for Ψ_σ (equation 66 of his memoir on Hypergeometric Series).

For very small values of $r-\rho$ the equation reduces to

$$U_0 = -\frac{5\pi}{6}B(r-\rho)^3(r+\rho). \quad . \quad . \quad . \quad (7\,c)$$

The value of U_1 is, according to equation (3 *b*), in this case

$$U_1 = \frac{A(r^2-\rho^2)}{4Lk^2},$$

and the equation $U_0+U_1=0$ gives therefore for very small values of $(r-\rho)$

$$-\frac{5\pi}{6}B(r-\rho)^2 = \frac{A}{4Lk^2}, \quad . \quad . \quad . \quad (7\,d)$$

or

$$P = \frac{6A}{5\pi(r-\rho)^2}.$$

In case the glass rod was fixed centrally we must put

$$u_0 = B(x^2+y^2-r^2) - B\frac{r^2-\rho^2}{\log r - \log \rho} \cdot \log \frac{\sqrt{x^2+y^2}}{r}, \quad . \quad (8)$$

and we obtain

$$U_0 = -\frac{\pi}{2}B(r^4-\rho^4) + \frac{\pi}{2}B\frac{(r^2-\rho^2)^2}{\log r - \log \rho}. \quad . \quad . \quad (8\,a)$$

For very small values of $\frac{r-\rho}{r}$ this will become

$$U_0 = -\frac{2\pi B}{6}(r-\rho)^3(r+\rho).$$

This is therefore only 0·4 of the value which U_0 presents when the glass fibre lies on the side of the tube. Corresponding to this the pressure-height, due to the electric propulsion of the liquid, will be 2·5 times higher for the central position of the rod than for its position against the wall.

Since, however, small bends in the rod may result in its lying in part centrally and in part along the wall, and moreover the small difference $r-\rho$ may be sensibly varied by very small irregularities in the diameters of the tube and fibre, we must not be surprised if the calculation does not agree very closely with Quincke's measurements. I have calculated the value of the inclination Δh_1 with enclosed glass fibre from the value Δh_0 for the empty tube which Quincke[*] gives in divisions of the scale he employed.

$2r$, mm.	2ρ, mm.	Δh_0.	Δh_1.	
			Found.	Calculated.
0·799	0·341	15·0	23·75	30·06
0·897	0·341	5·85	9·957	10·25
0·897	0·651	5·49	57·37	44·66
0·897	0·727	5·52	70·41	92·80

Although the agreement of single measured and observed values is, for the reasons given, not very perfect, yet the two show on the whole an agreement as to the general course of the function. For the least narrowed tube employed (line 2 in the table) the agreement is good; for the others the difference is sometimes positive, sometimes negative.

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[*] Pogg. *Ann.* cxiii. p. 544, table, 1861. In the last column of this table under nos. 5 and 7, before the two numbers beginning with 2, a zero is to be struck out, which, however, has nothing to do with the above calculation.

§ 3. *Transport of Water by the Discharges of Leyden Jars.*

In these investigations Quincke employed narrow tubes, which in two or more places were enlarged to receive the platinum wires which admitted the current. The force of the current then acted only on a part of the whole tube; but the liquid must have moved forward against friction throughout the length of the tube. Since under these conditions the velocity u_0 produced by the difference of hydrostatic pressure is proportional to this difference of pressure, we may, for shortness, write the equation from which the amount of fluid $U_{1,2}$ passing through the cross section in unit time is determined thus:

$$W_{1,2}U_{1,2}=P_1-P_2, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where P_1 and P_2 are the pressures at the beginning and end of the tube, and for cylindrical tubes of circular section and radius R,

$$W_{1,2}=\frac{8k^2L}{\pi R^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad *(9\,a)$$

expresses the hydrostatic frictional resistance of the tube.

Now let the beginning of the capillary tube, which projects into a larger vessel of water, be denoted by the suffix 1, the ends of the two platinum wires through which the current passes by 2 and 3, finally the end of the liquid column by 4; then electric transportation only occurs between 2 and 3, and the amount of it is, as shown above, if we put

$$\phi_i-\phi_a=\phi,$$

$$U=\frac{J\sigma}{4\pi k^2}\cdot\phi.$$

The quantity of fluid passing through a cross section of the tube must, however, be the same everywhere, therefore

$$U_{1,2}=U_{2,3}+\frac{J\sigma}{4\pi k^2\phi}=U_{3,4}. \quad . \quad . \quad . \quad (9\,b)$$

On the other hand, we may express the U's by means of the differences of pressure:

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* A misprint in the original is here corrected.

$$\frac{P_1-P_2}{W_{1,2}}=\frac{P_2-P_3}{W_{2,3}}+\frac{J\sigma}{4\pi k^2}.\phi=\frac{P_3-P_1}{W_{3,4}}. \qquad . \quad . \quad (9\,c)$$

The initial and final pressures are made equal, $P_1=P_4$. From the two equations the two unknown quantities P_2 and P_3 are determined :

$$\frac{P_1-P_2}{W_{1,2}}=\frac{P_3-P_1}{W_{3,4}}=\frac{W_{2,3}}{W_{1,2}+W_{2,3}+W_{3,4}}.\frac{J\sigma\phi}{4\pi k^2}=U_{1,2}=U_{3,4}. \qquad (9\,d)$$

Thence it follows that

$$U_{2,3}=-\frac{W_{1.2}+W_{3,4}}{W_{1,2}+W_{2,3}+W_{3,4}}.\frac{J\sigma\phi}{4\pi k^2}.$$

Within the tube (2, 3), therefore, the stream flows in the opposite direction to that in the surface layer, and to that in the end portions of the tube. This result was also arrived at by Quincke by observing the motion of small solid particles contained in the liquid*.

If we integrate with respect to time, then

$$\int J dt=E,$$

i. e., is equal to the quantity of electricity transported ; hence

$$\int U_{3,4}\,.\,dt=\frac{W_{2,3}}{W_{1,2}+W_{2,3}+W_{3,4}}.\frac{E\sigma\phi}{4\pi k^2}. \qquad . \quad . \quad (10)$$

Accordingly the displacement of fluid in the rise-tube, as Quincke calls the tube 3 to 4, is proportional to the quantity of electricity discharged, independently of its electromotive force, and increases proportionately to the specific resistance of the fluid, just as the above-named experimenter found. If there be three platinum wires in the tube, and we distinguish the middle one by the suffix 5, and the displacements in the rise-tube corresponding to each electric discharge by $H_{2,5}$, $H_{5,3}$, $H_{2,3}$, according as the wires 2 and 5, 5 and 3, or 2 and 3 are electrodes, then our equation gives

$$H_{2,5}+H_{5,3}=H_{2,3},$$

which Quincke also found by direct observation.

If, owing to the greater width of the tube, $W_{2,5}$ be smaller

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[*] Pogg. *Ann.* cxiii. p. 568 *sqq.*, 1861.

than $W_{5,3}$, the amounts transferred should be inversely proportional to the fourth power of the radius. The experiments (*loc. cit.* p. 528) gave a somewhat greater ratio than corresponds to the assigned radii of the tubes (namely, from 15 to 16 instead of 6, 9) for the transportation in the narrower tube. The reason possibly lies in the inequality of the inner surface, the ellipticity of the section, or in a circumstance to be mentioned immediately.

The hydraulic resistance W is sensibly increased by enclosed glass fibres. If one such be placed in $W_{3,4}$ the transportation sensibly diminishes, if in $W_{2,3}$ it sensibly increases, as our formula, in agreement with experiment, shows. For the rest, these methods of treatment hold only for those cases in which the discharge of the Leyden battery is delayed sufficiently long by an interposed column of distilled water to allow the setting up of a kind of flow nearly allied to stationary motion in the tube. In the case of very powerful discharges accompanied by sparks, the laws found above were no longer applicable ; the displacement was then smaller than it should have been. The displacement of solid particles suspended in water by powerful electric currents, observed by G. Quincke, is explained, as may be easily seen, by the same hypothesis.

According to the hypothesis just dealt with, a particle lying in the liquid would receive an electric charge of opposite sign to that of the liquid, as a rule negative, so that the negative part of the resulting double layer would reside on the solid particle, the positive on the liquid. Moreover the algebraical sum of the two quantities of electricity is zero, and the centre of gravity of the whole system of solid particle and electrically charged fluid layer taken together cannot therefore be displaced by the forces of electric attraction which arise from the fall of potential in the liquid through which the current passes. But these attractive forces would tend to bring about a displacement relatively to each other of the positively charged water-layer and the negatively charged particle, whereby the water-layer follows the current of positive electricity, while the particle moves in the opposite direction. If the fluid be a perfect insulator, then the new position would continue to exist as a position of equilibrium. Since, however, owing to the displacement of the layers, the equilibrium of the galvanic tension between the solid body and the fluid is destroyed, and is always endeavouring to restore itself by conduction, the first condition of electric distribution will always be again set up, and new displacements of the particle with respect to the surrounding water-layer will continually occur. Moreover it is clear that, with the small value of the velocity of the current thus set up, the velocity of the particle relative to the surrounding mass of water will be proportional to the magnitude of the force acting, *i. e.* to the electric current-density, or, if the tube be of uniform section, to the strength of the current.* At the same time, it is to be remembered that within the tube, as was shown above, a backward flow of fluid takes place which carries with it the suspended particles and likewise, under conditions otherwise similar, is proportional to the intensity of the galvanic current.

§ 4. *Electricity Transported by the Flowing Liquid.*

Let ϵ be the electric density at a distance N from the wall of the tube, the value of u at the wall being zero, then this last at distance N can be put equal to $\mathrm{N}\frac{\partial u}{\partial \mathrm{N}}$, and we obtain for the quantity of electricity carried with it by the fluid through an element of surface of the cross section of the tube, $ds\,.\,d\mathrm{N}$, in unit time the expression

$$\epsilon\frac{\partial u}{\partial \mathrm{N}}\,.\,\mathrm{N}\,.\,ds\,.\,d\mathrm{N}.$$

If we integrate with respect to N, then

$$\int\epsilon\,.\,\mathrm{N}\,.\,d\mathrm{N}=-\frac{1}{4\pi}\int_0^\infty\frac{\partial^2\phi}{\partial\mathrm{N}^2}\,.\,\mathrm{N}\,.\,d\mathrm{N}=\frac{1}{4\pi}(\phi_i-\phi_a),$$

the same quantity as would express the moment of the double layer, if the opposed electricity of the reservoir were all collected in the bounding surface. Accordingly we obtain for the quantity of electricity carried along by the fluid in unit time through the whole cross section of the tube :

$$\mathrm{E}_0=\frac{1}{4\pi}(\phi_i-\phi_a)\int\frac{\partial u}{\partial\mathrm{N}}\,.\,ds. \quad . \quad . \quad . \quad . \quad (11)$$

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* Quincke, Pogg. *Ann.* cxiii. p. 580, 1861.

According to Green's theorem,

$$\int \frac{\partial u}{\partial N} \cdot ds = -\iint \Delta u \, . \, dy \, . \, dz = -\frac{PQ}{k^2 L},$$

if, as above, we denote by P the difference of pressure between the ends of the tube, by L its length, by Q its cross section, and by k^2 the coefficient of friction of the fluid, and if, further, the conditions for u expressed in § 1 be complied with. Then is

$$E_0 = -\frac{PQ}{4\pi k^2 L}(\phi_i - \phi_a). \quad . \quad . \quad . \quad . \quad (11\,a)$$

If, in addition, an electromotive force A acts between the ends of the tube, the quantity of electricity transferred in unit time through each section by the electric current is

$$E_1 = \frac{AQ}{\sigma L}.$$

If no other conducting path be present save that through the tube, the condition will be stationary if

$$E_0 + E_1 = 0,$$

$$\frac{A}{\sigma} = \frac{P}{4\pi k^2}(\phi_i - \phi_a). \quad . \quad . \quad . \quad . \quad . \quad (11\,b)$$

This value of A is entirely independent of the length, size, and form of section of the tube. In a system of canals existing in the clay wall, A must therefore be independent of the thickness, area, and porosity of the plate, but proportional to the specific resistance of the fluid, if its chemical constitution undergoes no sensible change thereby. This agrees with Quincke's experiments. It is in this case assumed that the wall of the vessel may be looked upon as an insulator of electricity, compared with the flowing liquid (generally distilled water). For diaphragms of platinum, carbon, animal membranes pervious to water, or silk, this does not hold. Unfortunately, among the liquids employed by the above-named experimenter, none are included whose absolute resistance can be determined with certainty. Even in the investigation carried out with solutions of common salt* the solutions employed were so dilute that the proportionality of conductivity to salt-content is somewhat doubtful. In the case of solutions of somewhat better conductivity, the polarization of the platinum electrodes precludes exact measurement of the current-strength, and even of the electromotive force.

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* Pogg. *Ann.* cx. p. 59, 1860.

According to F. Kohlrausch*, the conductivity of a 5-per-cent. solution of common salt at 10° is equal to $523{\cdot}8 \times 10^{-8}$ if that of mercury be taken $=1$. The coefficient of friction may be deduced from that of water, as Quincke has given the quantity of liquid which the pressure drives through. The value of a Siemens unit of resistance in electrostatic measure is put equal to 10^{-12} sec.^{1} cm.$^{-1}$ In stating the value for the half-per-cent. solution of common salt, Quincke observes that in this case the want of uniformity of the electrodes is already so marked as to render the employment of solutions of greater concentration impossible. The calculation gives :—

Percentage of salt in solution.	$\phi i - \phi a$, in Daniells.
$\frac{1}{2}$	14·56
$\frac{1}{20}$	2·743
$\frac{1}{40}$	1·977
0	1·416 to 0·1416

In the last case I have put the conductivity of the distilled water, since it was not redistilled with special precautions, between 30×10^{-10} and 3×10^{-10} (mercury $=1$), in accordance with F. Kohlrausch's † results.

If we leave out of account the first value, which is obviously affected by the polarization of the electrodes, we find here again small electromotive forces between the wall and liquid, just as in the previous investigations.

§ 5. *Deviations in Wider Tubes.*

For the investigations in which water is allowed to flow, not through plates of clay, but through glass tubes, and the resulting difference of potential is measured, we must repeat that the theory given above assumes that the action of friction is completely developed throughout the whole tube, and that every single line of water moves as it would continue to move in an infinitely long tube. This assumption does not hold at the beginning of the tube, where the water enters it from a wider glass vessel. It arrives thither without possessing sensible motion of rotation. Within the tube, however, under the influence of friction, this is taken up. The rotations of the volume-elements, whose vortex-lines are concentric circles enclosing the axis of the tube, and the values of which, since $v=w=0$, reduce to $\frac{\partial u}{\partial y}$ and $-\frac{\partial u}{\partial y}$, are, farther inside the tube, no longer zero. A certain amount of time will therefore elapse before the entering water has attained the persistent stationary state of rotation of its vortex-filaments, and during this time it will have penetrated to a greater or less depth in the tube. Its duration may be calculated by a simple slightly different example.

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* *Göttinger Nachrichten*, 5 Aug. 1874.

† *Sitzungsber. der Münchner Akad.* 5 Nov. 1875.

We will suppose that the water is in an infinitely long tube in such a state of motion that u is a function of y and z only, p is independent of t, while

$$v=w=0,$$

whence it follows that

$$\frac{\partial p}{\partial y}=\frac{\partial p}{dz}=0.$$

The equation of motion, taking account of the friction, is accordingly

$$-\frac{1}{\epsilon}\cdot\frac{\partial p}{\partial x}=\frac{\partial u}{\partial t}-k^2\Delta u. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Since the left-hand side is independent of t, y, and z, and the right-hand of x, both must be constant, and u may be divided into two parts, such that

$$u=u_1+u_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (12\,a)$$

$$-\frac{1}{\epsilon}\cdot\frac{\partial p}{\partial x}=-k^2\Delta u_2; \quad 0=\frac{\partial u_1}{dt}-k^2\Delta u_1. \quad . \quad . \quad (12\,b)$$

Along the wall there applies to both the boundary condition

$$\bar{u}_1=\bar{u}_2=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12\,c)$$

Then u_2 is the finally persistent state of stationary motion which corresponds to Poiseuille's law.

To determine u_1 we have the same equations as if u_1 were the temperature in the cross section of a rod which is restored by conduction of heat to the condition $u_1=0$ which prevails permanently at the circumference of the tube. Thence it is easy to conclude that with lapse of time u_1 wholly vanishes, and the more quickly the narrower the tube and the greater the coefficient of friction k^2.

If the tube be of circular section we can develop u_1 by the aid of Bessel's functions. Putting

$$u_1=s\,.\,e^{-nt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

then

$$\frac{\partial u_1}{\partial t}=-n\,u_1=k^2\Delta u_1\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad (13\,a)$$

or, if s be a function of the radius ρ only,

$$\frac{\partial^2 s}{\partial \rho^2}+\frac{1}{\rho}\frac{\partial s}{\partial \rho}+\frac{n}{k^2}s=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13\,b)$$

Putting

$$\frac{n\rho^2}{k^2}=\sigma_1^{\,2},$$

the integral of equation (13 b), which is still continuous for $\rho=0$, is, as we know,

$$s=A\left\{1-\frac{\sigma^2}{2\,.\,2}-\frac{\sigma^4}{2\,.\,2\,.\,4\,.\,4}+\frac{\sigma^6}{2\,.\,2\,.\,4\,.\,4\,.\,6\,.\,6}-\;.\;.\;.\right\}. \quad (13\,c)$$

The values of σ for which $s=0$ determine therefore the values of n, if in the last equation but one the radius of the tube be put for ρ. The first value for which $s=0$ is

$$\sigma=\frac{\rho}{k}\sqrt{n}=2{\cdot}4048.$$

This gives the smallest value of n, namely for $k^2=1{\cdot}1445$ (at 15° C):

$$n=\frac{1}{\rho}\times 6{\cdot}6163\ \text{mm.}^2\ \text{sec.}^{-1}\text{*}$$

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* Calculation corrected on account of the misprint mentioned on p. 18.

If therefore $2\rho = 1$ mm., then

$$e^{-nt} = 0{\cdot}1$$

if $t = 0{\cdot}08701$ sec.

While, therefore, in a tube 1 mm. in diameter this, the part of the motion which diminishes most slowly, is reduced to $\frac{1}{10}$ of its value in about $\frac{1}{11}$ second, in a tube of diameter 2 mm. $\frac{4}{11}$ second would be necessary, in which case the liquid would, with the same velocity, have moved four times as far forward in the tube. An equal difference of pressure, however, produces in a tube twice as broad 4 times as much stationary velocity, and therefore 16 times as much forward motion, before an equal extinction of the motion under discussion takes place.

The second zero value of the Bessel's function is

$$\frac{\rho}{k}\sqrt{n}=5{\cdot}520.$$

The value thence arising for n is $5{\cdot}777$ times greater than the first, so that the second member of the Bessel's function would also vanish more rapidly in this proportion.

The behaviour in tubes through which water is continually flowing is naturally different from the behaviour just calculated in that the rapidly flowing middle layers come by degrees to lie upon such outer layers as have undergone the influence of friction in the tube during a longer period. If, moreover, the problem of the determination of such a flow is not directly soluble, the method of mechanical similarity helps us to obtain definite solutions. In the hydrostatic equations for viscous fluids, the first of which is

$$-\frac{1}{\epsilon}.\frac{\partial p}{\partial x}=\frac{\partial u}{\partial t}+u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}+w\frac{\partial u}{\partial z}-k^2\Delta u.$$

let us put :—

instead of x, y, z	$mx, my, mz,$
,, ,, $t,$	$nt,$
,, ,, $u, v, w,$	$qu, qv, qw,$
,, ,, $p,$	$rp,$

where m, n, q, r are constants. If u, v, w, p, are solutions of the equations, the substituted quantities will also be solutions, if

$$\frac{r}{m}=\frac{q}{n}=\frac{q^2}{m}=\frac{q}{m^2};\ i.\,e.\ \text{if}\ n=m^2,\ \ q=\frac{1}{m},\ \ r=\frac{1}{m^2}.$$

If, then, we increase m-fold all the linear dimensions of the tube, we can only obtain the same kind of flow if we diminish the velocities to $\frac{1}{m}$th and the difference of pressures to $\frac{1}{m^2}$th. Only in obedience to these rules can we expect to see the results of Poiseuille's law extend to wider tubes. That divergencies actually occur with increasing velocities in wider tubes I have previously shown in connexion with G. von Piotrowski's experiments [*]; the same thing can likewise be shown in the case of some of the investigations bearing on the present question.

Moreover, in the case of more rapid flow in wider tubes, the result may be largely modified by the form of the entrance to the tube. If the end of the tube be sharply cut off without any trumpet-shaped widening, then, as my [†] investigations and those of G. Kirchhoff [‡] have shown, the water may enter as a narrow moving stream surrounded by fluid relatively at rest. The originally sharp bounding surface between the two will in the first place be gradually transformed by friction into a rotating layer of finite thickness. Under these circumstances the motion at the wall and the differential coefficient $\frac{\partial u}{\partial N}$, which determines the electrical relation, would be at the commencement of the tube, or throughout if the tube be short, much smaller than in the stationary condition of vortex motion. On the other hand it is also possible, namely in the case of a funnel-shaped opening to the tube, that the bounding surface of the stream set in motion should attach itself to the tube-wall. In that case the quantity $\frac{\partial u}{\partial N}$ at the beginning of the tube must be much greater than in the course of a very long tube. We must therefore expect the full confirmation of the above formulæ only in the case of tubes so narrow, or pressures so moderate, that the law laid down by J. Poiseuille for the flow of water through capillary tubes is exactly complied with.

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[*] *Wien. Sitzungsber.* xl. pp. 654, 655, 1860; *Wissensch. Abh.* vol. i. p. 218.

[†] *Monatsber. d. Berl. Akad.* p. 215, 1868; *Wissensch. Abh.* vol. i. p. 146.

[‡] Crelle's *Journ. für r. u. angew. Math.* lxx. p. 289, 1869; *Vorlesungen über math. Physik.* (1), 22 Vorlesung.

Investigations into the dependence of the difference of potential produced by a current of water upon the other conditions have been made by Haga* and J. W. Clark †. Both used the quadrant-electrometer for the electrical part of the measurement. The first worked with distilled water, and confirmed the proportionality between the difference of potential and the hydrostatic pressure ; the second employed water from the Heidelberg water-supply and its constant pressure. Both investigations confirm the fact that the difference of potential is not dependent upon the length of the tube. In Haga's investigation the possible dependence of this difference of potential upon the width of the tube was covered up by effects due to chance inequalities on the inner surface of the tube. In the investigations of Clark, who employed the careful method for cleaning the tube given by Quincke, under whose direction he worked, the differences of potential which, according to our equation (11 *b*), should be constant, did not, as a matter of fact, differ very sensibly for all the narrow tubes (VI., II., III., VII.) of circular and elliptic section of from 0·2 to 0·7 mm. mean internal diameter, and even for one tube (I.*a*.) of 1·045 mm., although the fluid transmitted varied from 1·31 to 198·6 and 489·96 c. cm. per minute. For one tube (XX.) of 0·8 mm. diameter, and for those tubes which are wider than 1·4 mm., the differences of potential were much less.

If for the circular tubes the product be calculated

$$p=\frac{Q\,.\,l}{d^4},$$

where Q denotes the quantity of water flowing through per minute, l the length, and d the diameter of the tube, then, according to Poiseuille's law, this should be constant. The values are, however :—

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* Wied. *Ann.* ii. pp. 326–335, 1877.

† Id. pp. 335–346.

Number of the tube.	Diameter, mm.	Length, mm.	Q, cm.^{3}	$p\times 10^{-4}$.
II.	0·2952	226·5	5·0	14913
VII.	0·6918	112·3	198·6	9737
XX.	0·7952	142·1	155·5	5526
I. *a*.	1·045	203·9	489·96	8370
I.	1·413	224·6	994·75	5605
X.	7·67	335·0	24174·5	2337

The values of p show us that Poiseuille's law is complied with at most only in the case of the narrowest tubes. For elliptical tubes in which, according to Poiseuille's law, we must put

$$p=\frac{Q\,.\,l\,.\,(a^2+b^2)}{2a^3b^3},$$

the values do not at all agree, probably because the section of narrow thermometer-tubes is not regularly elliptical.

Clark divided the four narrowest tubes in half, and then found in them nearly, but not quite, the same amount of difference of potential, which should, according to equation (11 *b*), remain unaltered. However, only for the two narrowest was the efflux of water exactly doubled, as Poiseuille's law gives it.

In Haga's investigations the conditions are in some respects more favourable to compliance with the above-mentioned law. The diameter of the tubes lies between 0·3 and 0·7 mm. The tubes are longer and used under lower pressures (86 to 250 mm. by Haga as against 1285 mm. by Clark), so that even the wider tubes would have shown a smaller divergence than they did in the investigations of the latter observer. The absence of influence of length and the proportionality of the electromotive force are well brought out, but a further control by means of the amount of efflux is not offered.

Haga obtained for the magnitude of the electromotive force for commercial distilled water, under a pressure of 100 mm., between 0·5 and 0·9 Daniell; for water freshly distilled with great care as much as 4·5 Daniell. If we apply the above formula to this case we obtain as the lowest value of the potential-difference of the double layer occurring in water 3·5798 Daniell, somewhat greater than the values previously found. This would correspond to the lowest conductivity of distilled water, $0{\cdot}72 \times 10^{-10}$, compared with mercury, as obtained by F. Kohlrausch. Magnus's value 1·3 would give nearly twice, Quincke's value nearly three times as great a result.

If, instead of the difference of potential, the strength of the current flowing in a wire of good conductivity be observed, eliminating the polarization of the plates, as Edlund* has done, then the hypothesis developed by us, on the assumption of a flow obeying Poiseuille's law, gives results which are in many respects in agreement with those given by these researches, although Poiseuille's law be no better observed in this case. The latter is especially shown by the fact that the mean velocities in the case of the wider tubes were nearly proportional to the square roots of the pressures, and nearly independent of the widths of the tubes, so that friction obviously no longer exerted a preponderating influence on the flow.

The resistance of Edlund's galvanometer was vanishingly small compared with the resistance of the column of distilled water even in the widest tube, where this reached 1,824,000 ohms, and even with tap-water as much as 111,600 ohms. In these cases we may suppose that all the electricity brought to the electrodes flowed through them, and practically none backwards through the tube.

I will explain first the actions which must have occurred in a flow taking place according to Poiseuille's laws.

Let us put for a cylindrical tube

$$u = -A(x^2 + y^2 - r^2) = -A(\rho^2 - r^2), \quad . \quad . \quad (14)$$

then the discharge in unit time, as shown above, is

$$U = +\frac{A\pi r^4}{2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (14a)$$

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* Wied. *Ann.* i. p. 161, 1877.

therefore the mean velocity $\mathfrak{u}$ of the flowing liquid is given by the equation

$$\mathfrak{u} \,.\, \pi r^2 = \mathrm{U} = \frac{\mathrm{A}\pi}{2} \,.\, r^4,$$

therefore

$$\mathfrak{u} = \tfrac{1}{2} \,.\, \mathrm{A} r^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14b)$$

On the other hand,

$$\frac{\partial u}{\partial \mathrm{N}} = 2\mathrm{A}r = \frac{4\mathfrak{u}}{r}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14\,c)$$

therefore the quantity of electricity transported through each cross section in unit time is

$$\mathrm{J} = 2\mathfrak{u} \,.\, (\phi_i - \phi_a), \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14d)$$

i. e. the electric current is independent of the dimensions of the tube and proportional to the mean velocity of the flowing liquid. Its independence of the length and breadth of the tube with uniform mean velocity Edlund finds confirmed. But, on the other hand, he finds the electric current proportional rather to the square of the velocity (or to the pressure) than to the velocity in its first power.

I wish here to draw attention to the fact that for investigations of this kind the want of dependence of the action upon the diameter of the tube follows from the hypothesis of an electrification of the fluid against the wall of the vessel, and therefore cannot be used as an argument against this hypothesis, as Edlund does (*l. c.* p. 188).

If great resistances be included in the galvanometer-circuit a backward current must commence. If w be the resistance of the galvanometer, and w_1 that of the column of water, i and i_1 the corresponding current-strengths, then

$$iw = i_1 w_1; \qquad i + i_1 = \mathrm{J},$$

where J signifies as before the quantity of electricity carried to the electrodes by the motion of the water. Thence we obtain

$$i = \frac{\mathrm{J}w_1}{w + w_1};$$

so that, as Edlund again affirms, the conditions of the water-tube remaining the same, *i. e.* with the same values of J and w_1, the strength of the current in the galvanometer remains inversely proportional to the sum of the resistances of the entire circuit.

In Edlund's investigation the mean velocity varied from 8·3 to 11·5 m. per second. The water accordingly shot through portions of the tube of 140 to 280 mm. in length between the conducting-wires in $\frac{1}{80}$ to $\frac{1}{30}$ of a second. The wider tubes had diameters of from 5 to 6·4 mm. Under these circumstances it is to be supposed that only the outermost layers of water could be sensibly retarded by friction. The mean velocities found were in fact somewhat more than half as great as the velocities of efflux (14·23 and 20·13) answering to the pressure. Under these circumstances the differential coefficient $\frac{\partial u}{\partial N}$ must possess a far higher value than if through further action of friction the middle also of the stream had had its velocity diminished, and with greater velocities must be proportionally still greater. Thus the fact is probably explained that the water exhibits in wide tubes an electrical action which is nearly proportional to the square of the velocity; while in narrower tubes a proportionality to the first power, which is to be expected from theory, is actually found.

Moreover the two wider tubes give for distilled water, if we calculate according to formula (14 *d*), electric moments of 31 Daniell for the pressure of 1 atmosphere, 40·4 for 2; for spring-water 13·94 and 15·24 Daniell—values which are much higher than those already calculated. Under the given conditions this divergence in the numerical values is explained from the fact that the motion of the water does not correspond to Poiseuille's law, as is assumed in deducing equation (14 *d*).

That slipping along the walls does not exist we have been able to prove from Quincke's investigations on the transport of water in narrow glass tubes by means of the electric current. In that case the velocity of flow was very small, and the substance of the wall well wetted. There appears to me, however, to be no guarantee that the boundary-layer of the liquid would lie firmly fixed with greater velocities, or against substances wetted with difficulty, such as sulphur, shellac, &c. Piotrowski's memoir cited above demonstrates the fact that water against gold exhibits a definite amount of slipping. Directly slipping comes in, the propulsion of the electric boundary-layer will take place much more quickly than if the fluid clings firmly. In accordance with this, all the actions discussed would, with similar difference of tension against the surface of the wall, come in much more powerfully than in the case of the assumption made by us that $l=0$. Moreover the circumstance that many substances difficult to wet, as especially sulphur, show actions increasing with the time, may be connected with the fact that the liquid clings more feebly at first and more firmly afterwards.

ON THE

THERMODYNAMICS

OF

CHEMICAL PROCESSES.

BY

PROFESSOR H. VON HELMHOLTZ.

PART I.

Ueber die Thermodynamik der chemischen Prozessen. Sitzungsbericht der Akademie der Wissenschaften zu Berlin, 2nd February, 1882; also 'Wissenschaftliche Abhandlungen von H. Helmholtz,' vol. ii. pp. 958–978.

PREVIOUS investigations on the work-value of chemical processes relate almost exclusively to the quantities of heat appearing or vanishing during the formation and decomposition of compounds. Now alterations in the state of aggregation and in the density of the substances concerned are indissolubly connected with most chemical changes. Of these last, however, we know certainly that they are capable of producing or consuming work in two different forms, to wit: first in the form of heat, secondly in the form of other kinds of work convertible without limit. A store of heat is not, as is well known from Carnot's law—more precisely expressed by Clausius—convertible without limit into other work-equivalents. We can only bring this about in any case, and even then only partially, by allowing the untransformed residue of the heat to pass over into a body of lower temperature. We know that in the case of fusion, vaporization, expansion of gases, &c., heat can even be extracted from surrounding bodies at the same temperature, to pass over into work of other forms. Since such changes, as already said, are indissolubly connected with most chemical processes, this circumstance clearly proves that, even in the case of chemical changes, the origin of these two forms of work-equivalents must be examined, and they must be considered from the point of view of Carnot's law. It has long been known that there are chemical processes which occur spontaneously and proceed without external force, and in which cold is produced. Of these processes the customary theoretical treatment, which deals only with the heat developed as the measure of the work-value of the chemical forces of affinity, can give no satisfactory account*. They appear rather as processes which take place in opposition to the forces of affinity. In general, however, this view, which I have myself adopted in my earlier papers, is certainly justified. There is no question that, especially in those cases in which powerful forces of affinity act, the greater development of heat coincides with the stronger affinity, so far as the latter is to be recognized by means of the formation and decomposition of chemical compounds. But the two do not coincide in all cases. If we now take into consideration that chemical forces can produce not merely heat but also other forms of energy, the latter even without the necessity of any change of temperature in the interacting substances being set up corresponding to the magnitude of the effect, as, for example, in the case of the production of work by a galvanic battery; then it appears to me unquestionable that, even in the case of chemical processes, a distinction must be made between the parts of their forces of affinity capable of free transformation into other forms of work, and the parts producible only as heat. In what follows I shall, for the sake of brevity, distinguish these two parts of the energy as the "free" and as the "bound" energy. We shall see later that processes spontaneously originating and proceeding without the help of any external force, when the system is at rest and is maintained at a constant uniform temperature, can take place only in such a direction as to cause diminution of free energy. In this category will also be reckoned chemical processes originating spontaneously and proceeding at constant temperature. On the assumption of the unrestricted applicability of Clausius's law, it would therefore be the value of the free energy, not that of the total energy made known by development of heat, which especially determines the direction in which chemical affinity can become active.

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* B. Rathke, "On the Principles of Thermal Chemistry," *Abhandl. d. Naturforsch.-Ges. zu Halle*, Bd. xv.

As a rule the calculation of the free energy can be carried out only for such changes as are perfectly reversible in a thermodynamic sense. This is the case with many solutions and mixtures which, within certain limits, can be formed in all proportions. To such are related, *e. g.*, the researches on solutions of salts and gases undertaken by G. Kirchhoff*. On the other hand, among chemical combinations in the narrower sense, taking place by fixed equivalents, the electrolytic changes between unpolarized electrodes afford an important example of reversible processes. In fact, I myself have been led to the theory of free chemical energy, about to be set forth here, by the question of the connexion between the electromotive force of such a battery and the chemical changes going forward within it. Then also questions obtruded themselves as to how, whether, and when the latent heat of the gases developed during decomposition of water, or the heat set free during the crystallizing out of a salt produced by electrolysis, has or has not an influence on the electromotive force. The communication made by me, Nov. 26, 1877, "On Galvanic Currents originated by differences of Concentration" (*Wiss. Abh.* Bd. i. No. xliv.), falls clearly into this department.

In a constant galvanic element under the condition of a current-strength so vanishingly small that the development of heat in the connecting wire, proportional to the resistance and to the square of the current-strength, can be neglected as a vanishing quantity of the second order, the processes going on are perfectly reversible, and must obey the thermodynamic laws of reversible processes. If we have a galvanic element of uniform absolute temperature θ (*i. e.* temperature reckoned from $-273°$ C. as zero-point of the scale), its condition will be altered if the quantity of electricity $d\epsilon$ go through, owing to the fact that a chemical change occurs proportional to this quantity $d\epsilon$; and we can treat the state of the element as defined by the quantity ϵ of electricity which has traversed it in a definite direction assumed as positive. If the ends of the constant battery be connected with the two plates of a condenser of very great capacity which is charged to a difference of potential p, then the transfer of the quantity $d\epsilon$ from the negative to the positive plate of the condenser will correspond to an addition $p \,.\, d\epsilon$ to the store of electrostatic energy present. Let us denote at the same time by dQ the quantity of heat which we must communicate to (or, if negative, withdraw from) the galvanic element, in order to keep its temperature constant during the said transfer of $d\epsilon$, by U the total store of energy contained in it, which we can look on as a function of θ and ϵ, and by $\mathfrak{J}$ the mechanical equivalent of the unit of heat; then according to the law of the Constancy of Energy:—

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* Pogg. *Ann.* ciii. pp. 177 & 206, civ. p. 612.

$$\mathfrak{J} \,.\, dQ = \frac{\partial U}{\partial \theta} \,.\, d\theta + \left(\frac{\partial U}{\partial \epsilon} + p\right) . \, d\epsilon. \quad . \quad . \quad . \quad (1)$$

On the other hand, we shall obtain, according to the Carnot-Clausius principle, a function of the variables θ and ϵ, named by Clausius the entropy of the system, the variation dS of which is

$$dS = \frac{1}{\theta} . \mathfrak{J} . dQ = \frac{1}{\theta} \cdot \frac{\partial U}{\partial \theta} \,.\, d\theta + \frac{1}{\theta}\left[\frac{\partial U}{\partial \epsilon} + p\right] d\epsilon, \quad . \quad . \quad (1a)$$

whence

$$\frac{\partial S}{\partial \theta} = \frac{1}{\theta} \cdot \frac{\partial U}{\partial \theta}, \qquad \frac{\partial S}{\partial \epsilon} = \frac{1}{\theta}\left[\frac{\partial U}{\partial \epsilon} + p\right].$$

Thence it follows that

$$\frac{\partial^2 S}{\partial \theta \,.\, \partial \epsilon} = \frac{1}{\theta} \cdot \frac{\partial^2 U}{\partial \theta \,.\, \partial \epsilon} = \frac{1}{\theta}\left[\frac{\partial^2 U}{\partial \epsilon \,.\, \partial \theta} + \frac{\partial p}{\partial \theta}\right] - \frac{1}{\theta^2}\left[\frac{\partial U}{\partial \epsilon} + p\right],$$

or

$$\theta \,.\, \frac{\partial p}{\partial \theta} = \frac{\partial U}{\partial \epsilon} + p.$$

We can therefore now write equation (1) :—

$$\mathfrak{J} \,.\, dQ = \frac{\partial U}{\partial \theta} \,.\, d\theta + \theta \,.\, \frac{\partial p}{\partial \theta} \,.\, d\epsilon, \quad . \quad . \quad . \quad . \quad (1^{\circ})$$

wherein the last term gives the mechanical equivalent of that quantity of heat which we must supply to the galvanic element during the passage of $d\epsilon$ in order to keep its temperature constant. In fact, if in equation (1°) we put the variation of temperature $d\theta$ equal to zero, we have

$$\theta \cdot \frac{\partial p}{\partial \theta} \cdot d\epsilon = \mathfrak{J} \cdot dQ.$$

The quantity of heat developed in this way is in most cases relatively small, and with powerfully acting cells would be difficult to detect among the much greater quantities of heat which are proportional to the resistance of the conductor and the square of the current-strength. There are besides differences of heating at the two electrodes, which in their manner of appearance are similar to Peltier's phenomenon in the case of thermoelectric currents, even though they are perhaps of different origin. On the other hand, it may be ascertained much more easily, and with greater accuracy, whether the electromotive force of a constant galvanic element diminishes or increases with rise of temperature.

Investigations of the latter kind have been undertaken by Lindig *; unfortunately they chiefly refer to a case that is not strictly reversible, namely Daniell's cells in which the zinc is in contact with dilute sulphuric acid, which must therefore, when the current is reversed, develop hydrogen on the zinc. Really reversible Daniells, in which the zinc is in contact with zinc-sulphate solution, show, according to researches lately undertaken by me, a diminution of electromotive force with increasing temperature, if the zinc solution be of moderate or great concentration; an increase, on the contrary, in very dilute solution. Between these two alternatives there is a limit at which the electromotive force is sensibly independent of the temperature. With concentrated copper solution this occurs when the zinc solution has a specific gravity of about 1·04.

Latimer Clark's cells, in which a layer of mercurous sulphate in concentrated zinc [sulphate] solution lies on a mercury anode, and the kathode is formed of amalgamated zinc, are

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* Pogg. *Ann.* cxxiii. pp. 1–30, 1864.

specially adapted for accurate measurements, since the diffusion of two liquids is here avoided, and the whole can be completely sealed into glass. Their electromotive force depends on the temperature in a very remarkable manner. L. Clark* himself has asserted that the electromotive force diminishes by 0·06 per cent. for a rise of 1 degree C. The maximum of this variability occurs if powdered zinc salt be allowed to remain in contact both with the mercury among its sulphate and with the liquid zinc amalgam. I found this quantity 0·08 per cent.; with greater dilution of the zinc solution it diminished to 0·03; while, on the other hand, the electromotive force underwent considerable increase. The above formula allows us to see that in the case of this most concentrated solution the work given up as heat bears to that which appears in the electromotive force the same ratio as

$$\theta.\frac{\partial p}{\partial \theta} : p = 1 : 4{\cdot}2.$$

In this case the zinc sulphate newly formed by the current can no longer be dissolved, and its latent heat of solution is saved; accordingly there is a more powerful development of heat in the cell in spite of the weaker electromotive force. The discussion of the thermoelectric relations of solutions of crystallizable salts, which I propose to give later, shows besides universally that, in batteries of this type, diluting the solution must increase the electromotive force by an amount which increases with increasing temperature.

Batteries of a similar type, which I have frequently employed during the last year on account of their cleanliness and constancy for very small current-strengths, in which the mercurous sulphate of the Clark is replaced by mercurous chloride (calomel) and the solution of zinc sulphate by one of zinc chloride, show, on the contrary, with stronger dilution of the latter solution a real though small increase of the electromotive force, with rising temperature.

I adduce these facts since they show that very manifold relations are here apparent. The thermoelectric researches of Lindig, Bleekrode†, Bouty‡, and Gore § exhibit the abundance of such differences. If, for instance, we take a central glass vessel communicating with four side vessels by means of syphon tubes all filled with the same liquid, two of the side vessels being heated, the other two cold, and if A and a denote the differences of potential between the liquid in the central tube and two unpolarizable metallic electrodes of one kind, B and b those of two electrodes of another kind, A and B referring to the heated liquid, a and b to the cold; then the electrode A joined to a gives a thermoelement, as likewise does B joined to b. Again, A and B, when joined, form a galvanic battery of higher temperature, a and b one of lower temperature. If, now, the electromotive force

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* Proc. Roy. Soc. xx. p. 444.

† Pogg. *Ann.* cxxxviii. pp. 571–604.

‡ *Almeida Journ. de Phys.* ix. p. 229.

§ Proc. Roy. Soc. 1871, Feb. 23.

$$A-a>B-b,$$

then also

$$A-B>a-b$$

and

$$(A-B)-(a-b)=(A-a)-(B-b).$$

If, for example, A and a belonged to zinc amalgam, B and b to mercury covered with mercurous sulphate, all in the same zinc-sulphate solution, then I was able actually to verify the last equation by experiment.

In order to employ these and other facts safely, it appeared to me that in the first place the discussion of a somewhat generalized form of the general principles of thermodynamics was necessary, and a method of expressing them more suitable to the subject, desirable. This led to a simplified analytical treatment of their laws. I will at present limit myself to the exposition of these theoretical discussions.

§ 1. *Idea of Free Energy.*

Dynamics has attained a great simplification and generalization of its analytical developments by the employment of the idea of "potential energy" (the negative of which is termed "Force Function" by C. G. J. Jacobi, "Ergal" by Clausius, "Quantity of Tension-force" by Helmholtz). Hitherto, however, in the employment of this notion, changes of temperature have not as a rule been considered, either because the forces, the work-value of which was calculated, were entirely independent of temperature, *e. g.* Gravitation, or because the temperature could be looked on either as constant during the process investigated, or as a definite function of mechanical changes (*e. g.*, in the case of the transmission of sound as a function of the density of the gas). Of course the physical constants occurring in the value of the ergal, such as density, coefficients of elasticity, &c., may vary with temperature; and in this sense of course this quantity would be a function of the temperature. In that case, however, the constants of integration entering into the value of every ergal would have to be determined quite arbitrarily for every new temperature, and the passage from one temperature to the other could not be made. The means of doing this is nevertheless easily obtained from the two fundamental equations of thermodynamics set forth by Clausius.

This philosopher has limited himself in the first instance, in his published papers, to the case in which the state of the body is conditioned by the temperature and only one other parameter. The expression of the law for the case in which changes of different kinds can occur, in that the state of the body is conditioned by several other parameters besides the temperature, can be easily formed according to the same principle as applies in the case of a single one. In what follows I have denoted the absolute temperature by θ; the parameters defining the state of the body, but independent of each other and of the temperature, by $p_{\mathfrak{a}}$. Their number must be finite, but may be as great as we please.

Clausius employs for the setting forth of his general laws two functions of the temperature and of the one parameter retained by him, which he names the "Energy," U, and the "Entropy," S. These, however, are not independent of each other, but are connected together through the differential equation

$$\frac{\partial S}{\partial \theta} = \frac{1}{\theta} \cdot \frac{\partial U}{\partial \theta}.$$

It will be shown that these two can be expressed by means of differential coefficients of the ergal completely determined as a function of the temperature, so that the thermodynamical equations no longer require two functions of the variables, but only one, namely the ergal.

The function denoted by Clausius in his equations by W coincides with the ergal, so long as the temperature is unaltered; with varying temperature, however, it is more generally a many-valued function of the temperature and of the parameter. What G. Kirchhoff (*l. c.*) has termed "Quantity of Action" is the function U.

I assume in the first place a system of masses anyhow arranged, which all have the same temperature θ, and which all undergo the same temperature changes. The state of this system will then be completely determined by θ and a number of independent parameters $p_{\mathfrak{a}}$.

I denote, as Clausius does, by dQ the quantity of heat introduced by an infinitesimally small change in the state of the body, the internal energy by U. The law of the constancy of energy can be brought into the form

$$\mathfrak{J}\,.\,dQ = \frac{\partial U}{\partial \theta}\,.\,d\theta + \Sigma_{\mathfrak{a}}\left\{\left(\frac{\partial U}{\partial p_{\mathfrak{a}}} + P_{\mathfrak{a}}\right)dp_{\mathfrak{a}}\right\} \quad . \quad . \quad . \quad (1)$$

Here $\mathfrak{J}$ denotes the mechanical equivalent of the heat-unit, and $P_{\mathfrak{a}}\,.\,dp_{\mathfrak{a}}$ the whole of the freely convertible work produced by the variation $dp_{\mathfrak{a}}$, part of which can pass over to surrounding bodies, while part may be transformed into kinetic energy of the masses of the system. This latter is moreover to be treated as *external* work in contradistinction to the internal changes of the system.

The second law of the mechanical theory of heat asserts that

$$\int \frac{\partial Q}{\theta}\,.\,d\theta = 0,$$

if the final state of the body becomes again the same as the initial state was, and if the series of changes which the body has gone through is perfectly reversible. The latter condition requires, for a system of bodies the parts of which always have their temperatures equal among themselves, only that no fresh heat be produced at the expense of other forms of energy. The above requirement cannot be complied with under the conditions mentioned unless dQ/θ is the differential of a one-valued function depending only on the temperature and on the state of the body, *i. e.* on the parameters $p_{\mathfrak{a}}$, one of which Clausius has named "Entropy" and denoted by S.

Therefore

$$\frac{1}{\theta}\cdot dQ = dS = \frac{\partial S}{\partial \theta}\cdot d\theta + \Sigma_{\mathfrak{a}}\left\{\frac{\partial S}{\partial p_{\mathfrak{a}}}\cdot dp_{\mathfrak{a}}\right\}. \quad . \quad . \qquad (1\,a)$$

From (1) and (1 *a*) follow

$$\mathfrak{J}\cdot\frac{\partial S}{\partial \theta} = \frac{1}{\theta}\cdot\frac{\partial U}{\partial \theta}, \qquad \mathfrak{J}\,\frac{\partial S}{\partial p_{\mathfrak{a}}} = \frac{1}{\theta}\left[\frac{\partial U}{\partial p_{\mathfrak{a}}} + P_{\mathfrak{a}}\right].$$

Thence follows

$$P_{\mathfrak{a}} = \frac{\partial}{\partial p_{\mathfrak{a}}}\left[\mathfrak{J}\,.\,\theta\,.\,S - U\right]. \quad . \quad . \quad . \quad . \qquad (1\,b)$$

Further,

$$\mathfrak{J}\cdot\frac{\partial^2 S}{\partial \theta\,.\,\partial p_{\mathfrak{a}}} = \frac{1}{\theta}\cdot\frac{\partial^2 U}{\partial \theta\,.\,\partial p_{\mathfrak{a}}} = \frac{1}{\theta}\left[\frac{\partial^2 U}{\partial \theta\,.\,\partial p_{\mathfrak{a}}} + \frac{\partial P}{\partial \theta}\right] - \frac{1}{\theta^2}\left[\frac{\partial U}{\partial p_{\mathfrak{a}}} + P_{\mathfrak{a}}\right] \quad . \qquad (1\,c)$$

From the latter equation follows again

$$\theta.\frac{\partial P_{\mathfrak{a}}}{\partial \theta} = \frac{\partial U}{\partial p_{\mathfrak{a}}} + P_{\mathfrak{a}}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1\,d)$$

If now we put

$$\mathfrak{F} = U - \mathfrak{J}\,.\,\theta\,.\,S, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1\,e)$$

then $\mathfrak{F}$, like U and S, is a one-valued function of the quantities $p_{\mathfrak{a}}$ and θ. The functions U and S, which are only defined by the values of their differential coefficients, each contain an arbitrary additive constant. If we denote these by a and β, it follows that in the function $\mathfrak{F}$ an additive term of the form

$$[a - \beta\,.\,\mathfrak{J}\,.\,\theta]$$

remains arbitrary; in other respects this function $\mathfrak{F}$ is completely defined by equation (1 *e*).

The equations (1 *b*) fall therefore into the form

$$P_{\mathfrak{a}} = -\frac{\partial \mathfrak{F}}{\partial p_{\mathfrak{a}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1\,f)$$

i. e. *in all transformations taking place at constant temperature the function* $\mathfrak{F}$ *expresses the value of the potential energy or of the ergal.*

By differentiating equation (1 *e*) with respect to θ we obtain

$$\frac{d\mathfrak{F}}{d\theta}=\frac{\partial \mathrm{U}}{\partial \theta}-\mathfrak{J}.\mathrm{S}-\mathfrak{J}.\theta.\frac{\partial \mathrm{S}}{\partial \theta}.$$

Since, however, as already remarked in relation to (1 *a*),

$$\mathfrak{J}.\frac{\partial \mathrm{S}}{\partial \theta}=\frac{1}{\theta}.\frac{\partial \mathrm{U}}{\partial \theta},$$

our equation reduces to

$$\frac{\partial \mathfrak{F}}{\partial \theta}=-\mathfrak{J}.\mathrm{S}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1\,g)$$

whence, in consideration of (1 *e*), follows immediately

$$\mathrm{U}=\mathfrak{F}-\theta.\frac{\partial \mathfrak{F}}{\partial \theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1\,h)$$

These two equations therefore supply the values of the two functions U and S (Energy and Entropy according to Clausius) in terms of differential coefficients of $\mathfrak{F}$.

From them it follows that

$$\frac{\partial \mathrm{U}}{\partial \theta}=-\theta.\frac{\partial^2 \mathfrak{F}}{\partial \theta^2}=\mathfrak{J}.\theta.\frac{\partial \mathrm{S}}{\partial \theta}.$$

This is the above-mentioned connexion between the functions S and U by means of a differential equation, which is therefore immediately satisfied by our expression of them in terms of the function $\mathfrak{F}$.

With the parameters p_a maintained constant, equation (1) gives

$$\mathfrak{J}.d\mathrm{Q}=\frac{\partial \mathrm{U}}{\partial \theta}.d\theta.$$

The quantity $\partial \mathrm{U}/\partial \theta$ expresses therefore, even in our generalized case, the heat-capacity of the system with contant parameters (calculated for the whole of the masses belonging to the system taken together). We will denote this by Γ. Thus

$$\mathfrak{J}.\Gamma=-\theta.\frac{\partial^2 \mathfrak{F}}{\partial \theta^2}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1\,i)$$

Since Γ, like θ, is an essentially positive quantity, it follows from this that $\partial^2\mathfrak{F}/\partial\theta^2$ is essentially negative, and that therefore the quantities $(-\partial\mathfrak{F}/\partial\theta)$ and $(\mathfrak{F}-\theta\,.\,\partial\mathfrak{F}/\partial\theta)$ with increasing temperature and constant parameters must proceed to positively increasing values. These are the quantities $(\mathfrak{J}\,.\,S)$ and U.

We obtain further, for calculating the values of $\mathfrak{F}$ with increasing temperature and constant parameters,

$$\frac{\partial^2\mathfrak{F}}{\partial\theta^2}=-\mathfrak{J}\,.\,\frac{\partial S}{\partial\theta}=-\mathfrak{J}\,.\,\frac{1}{\theta}\,.\,\Gamma.$$

Since

$$\theta\,.\,\frac{\partial^2\mathfrak{F}}{\partial\theta^2}=\frac{\partial}{\partial\theta}\,.\left[\theta\,.\,\frac{\partial\mathfrak{F}}{\partial\theta}-\mathfrak{F}\right]=-\mathfrak{J}\,.\,\Gamma,$$

we obtain, by integration, for the difference of the two values of $\mathfrak{F}$ which correspond to the same system of parameters but to two different temperatures, distinguished by the suffixes 1 and 0,

$$\mathfrak{F}_1-\mathfrak{F}_0=\mathfrak{J}\left\{(\theta_0-\theta_1)S_0+\int_{\theta_0}^{\theta_1}\Gamma\left(1-\frac{\theta_1}{\theta}\right)d\theta\right\}. \qquad (1\,k)$$

The values of $\mathfrak{F}_0$ and S_0, to be chosen arbitrarily, constitute the two above-mentioned arbitrary constants.

For an interval of temperature such that within it Γ can be looked on as constant we should have

$$\mathfrak{F}_1-\mathfrak{F}_0=\mathfrak{J}\,.\,(\Gamma-S_0)(\theta_1-\theta_0)-\mathfrak{J}\,.\,\Gamma\,.\,\theta_1\,.\,\log\left(\frac{\theta_1}{\theta_0}\right). \qquad (1\,l)$$

Hence it results that the value of $\mathfrak{F}_1$, even for the absolute zero-point of temperature, $\theta=0$, would remain finite, even though the value of Γ remain finite up to that point; while the value of

$$\frac{\partial\mathfrak{F}}{\partial\theta}=-\mathfrak{J}\,.\,S_1$$

would be infinite at the limit $\theta=0$, unless at this limit the value of Γ, referred to absolute temperature, were vanishingly small. On the other hand, the product $(\theta_1\,.\,S_1)$ even with finite Γ will at the limit, $\theta=0$, become equal to zero.

In the calculation of the work of physical processes the indeterminateness of these two constants offers no disadvantage, since we always have to do only with the difference of the work-values corresponding to two different states and temperatures of the body. Since the quantity S, which, as to its dimensions, corresponds to a specific heat, increases for each quantity of heat communicated to the system, we will assume the value of S_0 always so chosen that the value of S remains positive for every attainable degree of cold. I shall therefore continue to employ the symbol $\mathfrak{J} . S$ as an essentially positive quantity, instead of the negatively marked value $(-\partial\mathfrak{F}/\partial\theta)$.

When the values $\mathfrak{F}_0$ and S_0 are adopted for a state of the body chosen as the normal condition, all values of $\mathfrak{F}$ are determinate, as the above shows, if the capacity Γ be known for a single system of values of the parameters, and the work from this to every other system can be calculated for each constant temperature.

For isothermal changes the function $\mathfrak{F}$ coincides, as we have seen, with the value of the potential energy for work-values convertible without limit. I propose therefore to style this quantity the "free energy" of the system of bodies.

The quantity

$$U=\mathfrak{F}-\theta\frac{\partial\mathfrak{F}}{\partial\theta}=\mathfrak{F}+\mathfrak{J}.\theta.S$$

can be distinguished, as before, as the "total (internal) energy;" possible *vis viva* of the masses of the system remains excluded from both $\mathfrak{F}$ and U, so far as it belongs to the freely convertible work-equivalents, and not to heat. Then we may distinguish the quantity

$$U-\mathfrak{F}=-\theta.\frac{\partial\mathfrak{F}}{\partial\theta}=\mathfrak{J}.\theta.S$$

as the "bound energy."

If we compare the value of the bound energy,

$$U-\mathfrak{F}=\mathfrak{J}.\theta.S$$

with equation (1 *a*),

$$dQ=\theta.dS,$$

it results that the bound energy expresses the mechanical equivalent of that quantity of heat which must be conveyed into the body at temperature θ in order to raise its entropy to the value S.

It is to be remarked that all these values of U, $\mathfrak{F}$, S express only their excesses above the values corresponding to the normal condition, to which we refer as the starting-point of the calculation, since we do not possess the data for going back to the absolute zero-point of temperature.

In this department, finally, we require an expression in order to clearly distinguish the quantity hitherto designated in theoretical mechanics as *vis viva,* or actual energy, from the work-equivalent of heat, which is itself to be regarded for the most part as *vis viva* of invisible molecular motions. I would propose to distinguish the first as "*vis viva of regular motion.*" I call that "regular motion" in which the components of velocity of the moving masses can be viewed as differentiable functions of the space-coordinates. "Irregular motion," again, would be that in which the motion of each single particle need bear no kind of similarity to that of its neighbour. We have every reason to believe that the motion constituting heat is of the latter kind; and in this sense the quantity of entropy should be distinguished as the *measure of the irregularity.* With our means of observation, gross as they are in comparison with molecular structure, only regular motion can be freely reconverted into other forms of energy*.

§ 2. *The Production of Work expressed by means of the Free Energy.*

After it has been settled how the function $\mathfrak{F}$ is to be formed, and how the two functions U and S are to be derived from it, it is easy also to express the two other quantities, dW and dQ, present in Clausius's equations, though they are no longer generally integrable.

In order to shorten the notation we will distinguish the variations which any function of the coordinates undergoes if the parameters $p_{\mathfrak{a}}$ change, but not the temperature, by the symbol δ, but the complete variation, in which the temperature also changes, by d. For any function ϕ of $p_{\mathfrak{a}}$ and θ therefore

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* Whether such conversion be impossible in view of the fine structure of living organic tissues appears to me to be still an open question, the importance of which in the economy of nature is obvious.

$$\delta\phi=\Sigma_{\mathfrak{a}}\left[\frac{\partial\phi}{\partial p_{\mathfrak{a}}}\delta p_{\mathfrak{a}}\right], \qquad d\phi=\delta\phi+\frac{\partial\phi}{\partial\theta}\,.\,d\theta.$$

Accordingly the freely convertible external work is

$$\begin{aligned} d\mathrm{W} &= \Sigma(\mathrm{P}_{\mathfrak{a}}\,.\,dp_{\mathfrak{a}})=-\delta\mathfrak{F} \\ &= -d\mathfrak{F}+\frac{\partial\mathfrak{F}}{\partial\theta}\,.\,d\theta=-d\mathfrak{F}-\mathfrak{J}\,.\,\mathrm{S}\,.\,d\theta. \quad . \quad . \quad (1\,m) \end{aligned}$$

The quantity of heat simultaneously flowing in would be, according to equation (1),

$$\mathfrak{J}\,.\,d\mathrm{Q}=d\mathrm{U}-\delta\mathfrak{F};$$

or, making use of the value of U found in (1 h),

$$\begin{aligned} \mathfrak{J}\,.\,d\mathrm{Q} &= d\mathfrak{F}-d\left[\theta\,.\,\frac{\partial\mathfrak{F}}{\partial\theta}\right]-\delta\mathfrak{F} \\ &= -\theta\,.\,d\left[\frac{\partial\mathfrak{F}}{\partial\theta}\right]=\theta\,.\,\mathfrak{J}\,.\,d\mathrm{S}, \quad . \quad . \quad . \quad . \quad . \quad (1\,n) \end{aligned}$$

as (1 a) and (1 g) give.

By these determinations of dQ and dW the fundamental equations of the system set forth in (1) and (1 a) are identically satisfied even for the case of several parameters, and with them also all the results deduced from them by Clausius and other physicists.

If we have to do with cyclic processes, we can calculate the work in the form taken from (1 m)

$$d\mathrm{W}=-d\mathfrak{F}-\mathfrak{J}\,.\,\mathrm{S}\,.\,d\theta. \quad . \quad . \quad . \quad . \quad (1\,m)$$

If the series of changes entered upon be of the special kind during which S can be exhibited as a one-valued function of θ, in some such form as

$$\mathrm{S}=\frac{\partial\sigma}{\partial\theta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where σ is only a function of θ, then

$$d\mathrm{W}=d\mathfrak{F}-\mathfrak{J}\,.\,d\sigma\,;$$

and since the right-hand side is a perfect differential, the left is so also, consequently for a series of changes returning upon itself

$$\int dW=0.$$

In this case it is therefore not necessary that, during return to the initial condition, exactly the same system of values of the parameters $p_{\mathfrak{a}}$ should exist for every value of θ as during departure therefrom, but only that for each value of θ the same value of S should always recur. So far the cyclic process without work has here a greater freedom than in the case of the single parameter.

On the other hand, it is in this case clear that

$$\int_1^2 dW=\mathfrak{F}_1-\mathfrak{F}_2,$$

even if equation (2) continues to hold during the alteration and

$$\theta_2=\theta_1,$$

but the parameters $p_{\mathfrak{a}}$ have different values at the end from those at the commencement.

The simplest case of equation (2) is that of the *adiabatic* variation

$$S=\text{const.}$$

Then

$$\int_1^2 dW=\mathfrak{F}_1-\mathfrak{F}_2+\mathfrak{J}\,.\,S\,.\,(\theta_1-\theta_2).$$

If the constant S_0 contained in the values of $\mathfrak{F}$ and S be so chosen that the value herein contained shall be $S=0$, then likewise the external work is given simply by the difference between the values of $\mathfrak{F}$ for the beginning and end of the change. It is then only needful to eliminate the temperature from the value of $\mathfrak{F}$ by means of the equation

$$\frac{\partial\mathfrak{F}}{\partial\theta}=0.$$

Work can therefore, as equation (1 *m*) shows, only be produced, even in the case of several parameters, by means of a complete cyclic process, if the integral

$$\int S\,.\,d\theta<0,$$

or

$$\int \theta \,.\, d\mathrm{S} > 0,$$

i. e. the rise of θ must chiefly take place with the smaller values of S, while the growth of S, or positive values of dQ, must accompany the higher values of θ. The values of the parameters can in that case undergo every kind of alteration compatible with the values of S determined for each value of θ.

Transformation of Free into Bound Work.

The value of the bound work, which I will denote by $\mathfrak{G}$, is

$$\mathfrak{G} = \mathfrak{J} \,.\, \theta \,.\, \mathrm{S};$$

its variation therefore

$$\begin{aligned} d\mathfrak{G} &= \mathfrak{J} \,.\, \theta \,.\, d\mathrm{S} + \mathfrak{J} \,.\, \mathrm{S} \,.\, d\theta \\ &= \mathfrak{J} \,.\, d\mathrm{Q} + \mathfrak{J} \,.\, \mathrm{S} \,.\, d\theta. \end{aligned}$$

On the other hand,

$$\begin{aligned} d\mathfrak{F} &= \delta\mathfrak{F} + \frac{\partial \mathfrak{F}}{\partial \theta} \,.\, d\theta \\ &= -d\mathrm{W} - \mathfrak{J} \,.\, \mathrm{S} \,.\, d\theta. \end{aligned}$$

That is, therefore, $\mathfrak{G}$ increases in the first place uniformly at the expense of the introduced heat dQ, secondly in the case of rise of temperature by the amount $\mathfrak{J} \,.\, \mathrm{S} \,.\, d\theta$ at the expense of the free energy. The free energy is diminished by this last amount and by the amount of the external work performed, as is shown immediately by the equation

$$-\frac{\partial \mathfrak{F}}{\partial \theta} \,.\, d\theta = \mathfrak{J} \,.\, \mathrm{S} \,.\, d\theta.$$

Thereby also the variation of $\mathfrak{F}$ which corresponds to the variation of θ maintains its significance as production of work, and the "*entropy*" S appears as *the heat-capacity for heat produced at the expense of the free energy during adiabatic change.*

In all *isothermal* changes, in which $d\theta = 0$, work is produced only at the expense of the free energy. The bound energy changes in that case at the expense of the incoming or outgoing heat.

In all *adiabatic* changes, in which $dQ=0$, work is produced at the expense both of the free and of the bound energy.

In all other cases we can regard the facts as if all external work were supplied at the expense of the free energy, all loss of heat at the expense of the bound energy, and finally during every rise of temperature in the system free energy were transformed into bound to the amount stated.

The last change can also occur even in the case of irreversible processes, through the transformation of free energy into *vis viva,* and of this, by friction-like processes, partly or wholly into heat. If the latter be the case,

$$dQ=dU$$

simply; accordingly the heat given up in passing from the initial state denoted by the suffix (1) to the final state denoted by (2) will be

$$\mathfrak{J}\,.\,Q=U_1-U_2.$$

This is the quantity determined by the investigations hitherto made into the absorption of heat during chemical processes, the temperatures in the initial and final states being the same. The free work in isothermal transformation, viz.

$$W=\mathfrak{F}_1-\mathfrak{F}_2,$$

is essentially different from this, and cannot therefore be found by merely determining the total evolution of heat, as I have already remarked in the introduction.

Condition of Equilibrium and Direction of Changes spontaneously occurring.

Since in the case of infinitesimally small changes the quantity $\delta\mathfrak{F}$ conditioned by the variation of the parameters alone comes into consideration for every production of freely convertible work, being wholly independent of the value of the simultaneously occurring temperature-change $d\theta$, we therefore obtain in the first place that, without access of reversible external work-equivalents, to which also the *vis viva* of regular motion would belong, a positive value of $\delta\mathfrak{F}$ increasing with the time δt cannot arise. Under such conditions the ratio $\delta\mathfrak{F}/\delta t$ can only be zero or negative. Persistence in the given state would thus be secured if for all changes of the parameters possibly occurring at the then existing temperature

$$\delta\mathfrak{F} \geqq 0.$$

If, through rise of temperature, a point can be reached at which $\delta\mathfrak{F}$ begins to pass through zero to negative values, the phenomenon of dissociation would here occur with chemical compounds. Below this point, however, $\delta\mathfrak{F}$ must increase with falling temperature, *i. e.* the differential coefficient

$$\frac{\partial}{\partial\theta}\left[\delta\mathfrak{F}\right] = \delta\left[\frac{\partial\mathfrak{F}}{\partial\theta}\right] = -\mathfrak{J} \, . \, \delta S$$

must have negative values, δS therefore must be positive. Since now, for $d\theta = 0$,

$$dQ = \theta \, . \, dS,$$

it results that all chemical compounds which dissociate at high temperatures must evolve heat, at least in the parts of the thermometric scale lying close under the dissociation temperature, if they are formed in a reversible manner, but must render heat latent if they be decomposed.

The reverse will be true of such as separate into their constituents in the cold, as *e. g.* solutions of crystallizable salts.

With these general results the above-mentioned observations on galvanic elements actually agree.

Finally, collecting together once more the essential relations of the function $\mathfrak{F}$, from which its physical significance and properties are derived, they are the following :—

1. All external reversible work corresponds to change of the function $\mathfrak{F}$ conditioned by change of the parameters :

$$dW = -\delta\mathfrak{F}.$$

2. The differential coefficient $\partial\mathfrak{F}/\partial\theta$ can only be changed by bringing up fresh heat dQ. By "fresh heat" I understand such as is either communicated from surrounding bodies,

or is freshly produced through the transformation of freely convertible work-equivalents into heat:

$$d\left[\frac{\partial\mathfrak{F}}{\partial\theta}\right]=-\frac{1}{\theta}\cdot\mathfrak{J}\cdot dQ.$$

In this case it is to be noticed that in transformation of dW into heat dQ,

$$dW=\mathfrak{J}\cdot dQ.$$

3. The differential coefficient

$$\frac{\partial^2\mathfrak{F}}{\partial\theta^2}=-\mathfrak{J}\cdot\frac{1}{\theta}\cdot\Gamma,$$

is necessarily always negative.

That Γ is necessarily positive is tacitly assumed in all thermodynamical investigations, but an essential condition for this is that only transfer of heat from bodies at a higher to those at a lower temperature can produce work.

If the relations to each other of several bodies or systems of bodies at different temperatures be dealt with, the function $\mathfrak{F}$ for each single one is entirely independent of that for the others. Their relations to each other are only given by the fact that they can reciprocally communicate free energy and heat *inter se*, and in the case of reversible processes both pass over unchanged in amount; in that of irreversible processes, as already noted, work can be transformed into heat. For such transferences the new condition of reversibility is added, according to which transfer of heat may take place only between bodies at the same temperature. In all these relations, no change is produced by the generalization here carried out and the changed mode of expressing principles.

Supplementary Appendix.—It has perhaps not been insisted on above with sufficient clearness, that the laws developed only hold if the parameters be so chosen that, if they be constant, change of temperature is not accompanied by any production of work.

ON THE

THERMODYNAMICS

OF

CHEMICAL PROCESSES.

BY

PROFESSOR H. VON HELMHOLTZ.

PART II.

Zur Thermodynamik der chemischen Prozessen. Sitzungsbericht der Akademie der Wissenschaften zu Berlin, 27th July, 1882; 'Wissenschaftliche Abhandlungen von H. Helmholtz,' vol. ii. pp. 979–992.

IT was my desire to undertake exact experimental tests, quantitatively carried out on suitable examples, of the thermodynamical theorems which, in my communication made to the Academy on February 2nd of this year *, I had deduced from the second axiom of the mechanical theory of heat. The number of cases suitable for this is hitherto not very great. In order to test the applicability of the theorem, the chemical change concerned must be capable of being applied, in at least two ways, to an exactly measurable and reversible production of work. This is possible in the case of change of concentration of solutions. Such a [change] can be brought about by evaporation, or by condensation of vapour, and moreover by electrolysis.

That the difference in the electromotive force of galvanic elements, brought about through difference in the concentration of the salt solutions employed as electrolytes, can be calculated thermodynamically from the vapour-tensions of these solutions, has been shown already by the experiments

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[* *Ante*, p. 43.]

of James Moser, which he undertook with a view to testing* my theorems communicated to the Academy Nov. 26, 1877. But in these examples the result is essentially dependent on the velocity with which the electric transportation of the different constituents in the fluid proceeds. Thereby a further complication is introduced, which must be brought under calculation, and on the magnitude of which, especially in concentrated solutions, but few series of measurements sufficiently complete for our purpose have hitherto been carried out. We can, however, free ourselves from the intervention of this process if we employ galvanic elements, with one fluid and an insoluble depolarizing substance, such as have been prepared by Leclanché, Pincus, Warren de la Rue, Latimer Clark, &c. These batteries, to which also belongs the calomel battery mentioned in my last communication, are certainly not adapted for giving strong continuous currents; but they are in part very well suited to the measurement of electromotive forces by Poggendorff's compensation method, since in this case they are only employed without current. The calomel battery suggested by me can also be very conveniently used in such experiments for producing the compensating current. The constituents of such a battery are:—

Zinc,
Zinc chloride solution (containing 5 to 10 per cent. of the salt),
Calomel, finely powdered,
Mercury.

Two such elements connected together abreast give, in a circuit of 10,000 Siemens units of resistance, a current which may last for months without sensible polarization of the electrodes, and which, by the employment of a very sensitive galvanometer, is sufficient to allow us to recognize a difference of one millionth of the electromotive force of a Daniell's element. The electromotive force of this battery is very little influenced by fluctuations of temperature (it increases by about 0·0002 of its amount for [a rise of] 1° C.), and its resistance is infinitesimal compared with that of 10,000 Siemens units. After the passage of strong currents polarization is certainly present; [the cell] is likewise disturbed by mechanical shaking, whereby the surface of the mercury is partly expanded, partly contracted, and the electromotive forces observed by G Lippmann make their appearance. But in elements which contain more than five per cent. of $ZnCl_2$ in solution, these disturbances vanish as a rule in five to ten minutes. With still more strongly diluted solutions the elements become so sensitive to shaking that the magnet of the galvanometer, at least here in Berlin, continuously moved restlessly backwards and forwards under the influence of vibrations proceeding from the streets.

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* Wied. *Ann.* iii. pp. 216–219; xiv. pp. 62–85.

Since zinc chloride is that one of the salts suited for galvanic elements for solutions of which the most complete series of observations of vapour-tension exists, I have in the first place submitted to measurement the calomel elements described. In the course of the investigation some difficulties certainly presented themselves, which would require for their complete solution the help of an observer more skilled in chemical work.

Calculation of the Free Energy in Salt Solutions.

A current, which flows in the direction in which the electromotive force of these elements tends to excite it, dissolves zinc, while an equivalent quantity of calomel is reduced and gives up its chlorine. Freshly-formed zinc chloride, $ZnCl_2$, therefore appears, which passes into solution. On the other hand, undissolved solid mercury salt, Hg_2Cl_2, is decomposed into Hg_2, which mixes with the rest of the mercury, and Cl_2, which passes to the zinc. On the contrary, in the case of a current in the reverse direction, zinc is reduced from solution and fresh mercurous chloride formed. With different concentration of the liquid nothing is changed in these processes, except that the freshly-formed zinc chloride enters a solution of different concentration, or, on the other hand, that it is separated from such a [solution]. Beside the chemical forces, therefore, which favour the formation of zinc chloride at the expense of the calomel, those which tend to convey the zinc chloride when formed into the aqueous solution have to be considered; these, as might be supposed *à priori*, are more active in dilute solutions than in the more concentrated. In fact experiments at once show that the more dilute solutions give the elements of greater electromotive force.

If, as happened in the experiments, two elements with solutions of different concentration be opposed to each other, a current passing through both will form in one as much $ZnCl_2$ as is decomposed in the other, and in the first decompose as much Hg_2Cl_2 as is formed in the other. But if zinc chloride pass into a more dilute solution, and the same quantity be separated from a more concentrated solution, this is a process which can do work, and can therefore, like electromotive force, excite a current. This process is moreover perfectly reversible for a current-strength so small that the development of heat in the circuit proportional to the square of the current vanishes, and only quantities proportional to the first power of the current-strength are to be regarded.

Now we can change the concentration of such solutions also in a second perfectly reversible manner, namely, by evaporation.

Let w be the quantity of water in a solution of a salt, and s the quantity of salt. In order to separate the two constituents from each other an expenditure of work is necessary, and indeed an equal expenditure for every milligram of solution, though it may vary with the concentration. Let us put

$$\frac{w}{s} = h, \quad \ldots \ldots \ldots \quad (1)$$

then the expenditure of work for each unit of mass must be a function of h, which we will denote by F_h; therefore for the whole solution the free energy corresponding to its formation will be :—

$$\mathfrak{F} = (w+s)\,F_h, \quad \ldots \ldots \quad (1\,a)$$

or, in consideration of equation (1),

$$\mathfrak{F} = s\,(1+h)\,F_h. \quad \ldots \ldots \quad (1\,b)$$

If we allow the quantity of water to change by evaporation or condensation of water, while s remains constant, we shall have

$$\frac{\partial \mathfrak{F}}{\partial w} = s\frac{\partial}{\partial h}\Big[\,(1+h)\,F_h\,\Big]\cdot\frac{\partial h}{\partial w},$$

or, in consideration of the value of h,

$$\frac{\partial \mathfrak{F}}{\partial w}=\frac{\partial}{\partial h}\Big[(1+h)\mathrm{F}_h\Big]. \quad . \quad . \quad . \quad . \quad . \quad (1\,c)$$

This quantity multiplied by dw gives the work which must be supplied for every reversible transfer of the quantity of water dw from pure water to the solution, the temperature being maintained constant. If we denote by p the pressure of the vapour, by v the volume of its unit of mass, then we must put

$$\frac{\partial \mathfrak{F}}{\partial w}=-\int_{h=\infty}^{h=h} p\,.\,dv. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The small changes in volume of the liquids are therein neglected, since these vanish in comparison with the volume of vapour in the cases here considered. Moreover there is no difficulty in completing the formulæ in this respect.

If we denote the values of p and v in equation (2) which correspond to the saturation-pressure of pure water, *i. e.* to the value $h=\infty$, by P and V, then we have to distinguish three periods in calculating the integral in equation (2). In the first place we must allow the quantity of water dw* to evaporate from pure water; this gives, as the corresponding amount of the above integral, the work

$$\mathrm{P.V.}\ dw.$$

Then we must allow the vapour to expand further, out of contact with water, until it attains the specific volume v_h of the vapour overlying the salt solution; this contributes to the integral the amount

$$dw\int_{\mathrm{V}}^{v_h} p\,.\,dv.$$

Finally, the vapour is to be compressed in contact with the salt solution under the pressure p_h kept constant. This gives the final amount

$$-p_h\,.\,v_h\,.\,dw.$$

Accordingly,

$$\frac{\partial \mathfrak{F}}{\partial w}=-\mathrm{P.V}-\int_{\mathrm{V}}^{v_h} p\,.\,dv+p_h\,.\,v_h\ ;$$

or, by partial integration,

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* [Misprinted in the original as dW.—E. F. J. L.]

$$\frac{\partial \mathfrak{F}}{\partial w} = \int_{P}^{p} v\,.\,dp = -\int_{h}^{\infty} v\,.\,\frac{\partial p}{\partial h}\,.\,dh.\,. \quad . \quad . \quad (2\,a)$$

Since, according to equation (1*c*), $\partial\,\mathfrak{F}/\partial w$ is a function of h only, and on the right-hand side p and v are likewise only functions of h, equation (2 *a*) can be differentiated with respect to h, and gives

$$\frac{\partial^2}{\partial h^2}\Big[(1+h)\,F_h\Big] = v_h\,.\,\frac{\partial p}{\partial h}. \quad . \quad . \quad . \quad (2\,b)$$

According to the analysis in §1 of my first contribution, the quantity $-\partial\,\mathfrak{F}\,/\,\partial w$ is to be distinguished as *the force with which the water of the solution is attracted.* Equation (2 *a*) shows how to calculate its amount from the vapour-pressure.

On the other hand, by partial differentiation with respect to s, we obtain from equation (1 *b*)

$$\frac{\partial \mathfrak{F}}{\partial s} = (1+h)\,F_h - h\frac{\partial}{\partial h}[(1+h)\,F_h]. \quad . \quad . \,(1\,d)$$

If a galvanic current of strength J flow through one of our elements, and q denote that quantity of salt dissolved by means of the unit current in unit time, then in t seconds the store of energy present will be increased owing to solution of the salt by

$$\frac{\partial \mathfrak{F}}{\partial s}\,.\,J\,.\,q\,.\,t = J\,.\,q\,.\,t\,.\left\{(1+h\,.\,F_h) - h\,\frac{\partial}{\partial h}\,[(1+h)F_h]\right\}.$$

Now the work which an electromotive force A does, if a current J flow through the conductor during time t in the direction in which A acts, is equal to A . J . t, assuming that the unit of A is selected so as to correspond with this definition.

I will in what follows calculate by amperes and volts; but in that case the work of the vapour must also be calculated in the corresponding units, namely, 10^{-9} cgr.* for mass, 10^{9} cm. for length, and seconds for time. The work of the vapour calculated in C.G.S. measure is therefore to be multiplied by 10^{-7} in order to reduce it to this measure.

From equation (2 *b*) therefore it follows that

$$A = -q\left\{(1+h)\,F_h - h\frac{\partial}{\partial h}\;[(1+h)\;F_h]\right\}; \quad . \;(2\,c)$$

and in consideration of equation (2),

$$\frac{\partial A}{\partial h} = q\,.\,h\,.\,\frac{\partial^2}{\partial h^2}[(1+h)\,F_h] = q\,.\,h\,.\,v\,.\,\frac{\partial p}{\partial h}. \quad . \;(2\,d)$$

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* [Or 10^{-11} grammes.]

The sign is here so chosen that a current dissolving the metallic base of the salt and the electromotive force acting in its direction are simultaneously given as positive.

If we have separation of salt in one cell with the dilution-value h_0, and solution in another of value h_1, then we get from equation (2 *d*), by integrating with respect to h,

$$A_1 - A_0 = q\int_0^1 h \cdot v \cdot \frac{\partial p}{\partial h} \cdot dh. \quad . \quad . \quad . \quad . \quad (2\,e)$$

This equation allows us to calculate from the vapour-tensions the electromotive forces corresponding to the difference of the [amounts of] water contained in the solution.

Since at temperatures below 40° the density even of the saturated vapour of pure water is very small, we can accordingly determine the quantity v by means of the laws of perfect gases, and if we denote by V_0 and P_0 the magnitudes of v and p for pure water at the absolute temperature Θ, we can put

$$\frac{P_0\,V_0}{\Theta} = \frac{p.v}{\theta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$A_1 - A_0 = \frac{\theta . q . P_0 V_0}{\Theta}\int_0^1 h \cdot \frac{\partial \log p}{\partial h} \cdot dh \quad . \quad . \quad (3\,a)$$

Since for zinc chloride no investigations on the vapour-tension at different temperatures exist, it is useful to note the following relations.

If we differentiate equation (2 *d*) with respect to the absolute temperature θ we obtain

$$\frac{\partial^2 A}{\partial h \, . \, \partial \theta} = q \, . \, h \, . \, \frac{\partial^2}{\partial h^2}\left[(1+h)\,\frac{\partial F_h}{\partial \theta}\right]; \quad . \quad . \quad (4)$$

and if we multiply (4) by θ and subtract it from (2 *d*), it gives

$$\frac{\partial}{\partial h}\left(A - \theta\,\frac{\partial A}{\partial \theta}\right) = q \, . \, h \, . \, \frac{\partial}{\partial h}\left[\frac{\partial \mathfrak{F}}{\partial w} - \theta \, . \, \frac{\partial^2 \mathfrak{F}}{\partial \theta \, . \, \partial w}\right], \quad . \quad (4\,a)$$

as to which it is to be noted that $\partial\mathfrak{F}/\partial w$, and therefore also its differential coefficient with respect to θ, contains the quantities w and s only implicitly in h. But now, as was shown in the earlier essay*,

$$\mathfrak{F} - \theta\,\frac{\partial \mathfrak{F}}{\partial \theta} = U,$$

and U is the total internal energy, free and bound taken together. Accordingly $\partial U/\partial w$ is likewise a function of h only, and $\partial U/\partial w \, . \, dw$ denotes the mechanical equivalent of the quantity of heat, which must be communicated to the solution during the addition of the quantity of water dw in order to keep the temperature of the solution constant, whether the water be added directly without production of external work or subject to the reconversion of the latter into heat.

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* [*Vid. supr.* p. 55.]

Let us put therefore $-\partial U/\partial w = W$, then W is the quantity of heat to be developed by dilution with unit weight of water, likewise only a function of h and θ, and equation (4 *a*) will become

$$\frac{\partial}{\partial h}\left(A - \theta\frac{\partial A}{\partial \theta}\right) = -q \, . \, h \, . \, \frac{\partial W}{\partial h}. \quad . \quad . \quad . \quad (4\,b)$$

Thence it follows that, in the case of solutions which on further dilution neither evolve heat nor render it latent, the parts of the electromotive force dependent on the concentration of the solution must increase proportionally to the absolute temperature, since in that case we shall have

$$\frac{\partial A}{\partial h} = \theta \, . \, \frac{\partial^2 A}{\partial \theta \, . \, \partial h},$$

or we must have

$$d\,(\log \theta) = d\left(\log \frac{\partial A}{\partial h}\right),$$

$$\frac{\partial A}{\partial h} = C\theta.$$

Since for pure water ($h = \infty$), W will be $= 0$, the quantity W itself is with negative values of $\partial W/\partial h$ necessarily positive, and *vice versâ*. Therefore if dilution evolve heat, $\partial A/\partial h$ will necessarily increase more slowly, in the opposite case more rapidly, than the absolute temperature.

Let us insert assumption (3) into (2 *d*), then we shall obtain

$$\frac{\partial A}{\partial h} - \theta\frac{\partial^2 A}{\partial h . \partial \theta} = q \, . \, h \, . \, \frac{V_0 P_0}{\Theta} \, . \, \theta^2 \frac{\partial^2}{\partial h \, . \, \partial \theta}(\log p) = -q \, . \, h \, . \, \frac{\partial W}{\partial h}.$$

Therefore

$$-\frac{\partial W}{\partial h} = \frac{V_0 P_0}{\Theta} \, . \, \theta^2 \, . \, \frac{\partial^2}{\partial h \, . \, \partial \theta} \, . \, (\log p).$$

This integrated with respect to h up to $h = \infty$, where W must be $= 0$, gives

$$W = \frac{V_0 P_0}{\Theta} \cdot \theta^2 \cdot \frac{\partial}{\partial \theta}\left[\log\frac{P}{p}\right], \quad . \quad . \quad . \quad . \quad (4\,c)^*$$

which equation allows us to calculate the heat of dilution from the temperature-variations of the vapour-tensions, or the latter from the former.

On the Calculation of the Experiments.

For dilute salt-solutions, Wüllner has found approximately

$$P - p = \frac{b}{h} \cdot P, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where b denotes a constant depending on the nature of the salt, which with some salts appears independent even of the temperature. This, put in equation (3 a), would give

$$A_1 - A_0 = \frac{\theta P_0 V_0}{\Theta} \cdot qb \log\left[\frac{h_1 - b}{h_0 - b}\right] \quad . \quad . \quad . \quad . \quad (5\,a)$$

With chloride of zinc relatively high concentrations can be employed, for which Wüllner's simple formula, equation (5), is no longer sufficient. A formula of the second degree corresponds very well with James Moser's series of observations on the vapour-tension of zinc-chloride solutions :

$$P - p = \frac{\mathfrak{A}}{h} + \frac{\mathfrak{B}}{h^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

From this the value of p may be brought into the form

$$p = \mathfrak{B}\left[\frac{1}{a} + \frac{1}{h}\right]\left[\frac{1}{\beta} - \frac{1}{h}\right],$$

in which $-a$ and β are the values of h which in equation (6) would give the value $p=0$. Thence we obtain

$$A_1 - A_0 = \frac{q \cdot P_0 \cdot V_0 \cdot \theta}{\Theta}\left\{\beta \log\left(\frac{h_1 - \beta}{h_0 - \beta}\right) - a \log\left(\frac{h_1 + a}{h_0 + a}\right)\right\} \quad . \quad (6\,a)$$

I have calculated the coefficients $\mathfrak{A}$ and $\mathfrak{B}$ from Moser's observations by the method of least squares, and found the values

$$\mathfrak{A} = 4 \times 17{\cdot}1608,$$
$$\mathfrak{B} = 16 \times 1{\cdot}9559.$$

The comparison of the calculated values based thereon with the observations gives in millimetres of water-pressure at 20°·2 C.:—

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* In (4 c) and the two previous equations θ stands incorrectly in the original [*Monatsber.*] in place of θ^2.

$4\times\frac{1}{h}$.	P−*p*.		Difference.
	Calculated.	Observed.	
1.	19·127	19·50	+0·373
2.	42·145	39·83	−2·315
3.	69·085	69·87	+0·785
4.	99·938	101·90	+1·962
5.	134·701	133·60	−1·101

The value of P, in accordance with Magnus's table of vapour-tensions, is put equal to 239·79 millim. of water at 20°·2 C. Thence, and from the values of $\mathfrak{A}$ and $\mathfrak{B}$, are obtained the values of

$$\alpha=0{\cdot}24545,$$
$$\beta=0{\cdot}53171.$$

For one ampere q is, in accordance with F. Kohlrausch's most recent determinations, 0·0011363 grm. per second relative to silver, therefore relative to $ZnCl_2$ 136/216 times this amount, viz.:

$$q=0{\cdot}00071545.$$

The theoretical value of P_0V_0 at 0°, applicable for very small densities of water-vapour is, expressed in C.G.S. measure,

$$P_0\,.\,V_0=1{\cdot}25985\times10^9.$$

I shall specify the values of the electromotive force calculated from the above interpolation-formula (6), combined with the given values of $\mathfrak{A}$ and $\mathfrak{B}$ as "calculated from *a*." Since in the comparison of the calculated and observed vapour-tensions, as they are given above, certain differences present themselves (*e. g.* in the case of (2) and (4)) which are greater than those of Moser's observations *inter se*, and since the formation of hydrates of the salt may possibly condition a different course of the function for different concentrations, I have undertaken a second calculation, in which I have applied a formula formed like (6) to each three consecutive observed values between which the concentration considered of the element dealt with lay. The values thence arising I shall distinguish as "calculated from *b*." The two calculations differ for the smaller intervals very perceptibly from each other. But the sum agrees very well for the electromotive force of the larger intervals.

The great tendency of zinc chloride to form basic salts forms an obstacle to exact carrying out of the measurements. The normal solution, by diluting which the other concentrations were formed, must be so chosen that zinc will no longer dissolve with evolution of hydrogen in the elements at the temperature of the room, for which purpose it must contain a little basic zinc chloride. And, on the other hand, it must not contain so much of the latter as to give a precipitate of strongly basic salt on dilution with considerable quantities of water. These two conditions give rather narrow limits for the composition of the liquid. My solution contains, according to the determination of its contained zinc and chlorine, in 100 grms.,

63·736 grm. $ZnCl_2$,
0·881 grm. ZnO,
35·383 grm. H_2O.

I think I may assume that Moser's solutions were of a similar kind, chloride solutions saturated cold with zinc, since he must have observed in his experiments the same two conditions as myself. Unfortunately, he has given no information in his publication on this point, or as to the way in which he determined the concentration of the solutions.

The value of the calomel element in volts was determined by ascertaining its electrolytic equivalent, by means of a resistance measured in Siemens units. Since I had assumed the electrochemical equivalent of silver from F. Kohlrausch's measurements, it appeared to me safest to assume the value of the Siemens unit of resistance belonging thereto, determined by the same observer, viz. 0·9717 of the theoretical ohm. The electromotive force of my compensating calomel element, working through 10,000 resistance units, was thus found to be 1·043 volt. But since the determinations hitherto made, by the best experimenters, of the absolute value of the Siemens unit differ from each other by about 3 per cent., and therefore the value of my elements would be but uncertainly expressible in volts, I have finally preferred to reduce the calculated values to the electromotive force of my calomel element.

Since, in addition to these sources of uncertainty, small inequalities of the different zinc rods appeared to be established, which had a relatively important influence on the values of the smaller intervals, it will be sufficient to give here the results for the greatest interval of concentration, which it was practicable to employ between $h=0{\cdot}8$ and $h=9{\cdot}1992$, between 17°·7 and 21° C.

Electromotive Force.

Observed	Maximum	0·11648
	Minimum	0·11428
Mean of 13 days		0·11541
Calculated	*a*	0·11579
	b	0·11455

Moreover, I have had a thermostat constructed, in which the six different elements to be compensated could be enclosed. Between 35°·1 and 36°·1 C. was observed :—

Maximum	0·11609
Minimum	0·11524
Mean of 8 days	0·11569

Thence we obtain that the part of the electromotive force depending on differences of concentration scarcely alters at all with the temperature.

The $\partial^2 A/\partial\theta\,.\,\partial h$ of equation (4 *b*) is therefore approximately zero, whence it follows that $\partial W/\partial h$ must be negative. Since $\partial A/\partial h$ is positive, and since W will necessarily be equal to zero for $h=\infty$ (*i. e.* for pure water added to pure water), W must then be positive for all solutions of zinc chloride. Addition of water must evolve heat. Preliminary experiments have already proved to me that this is the case, and even nearly to the extent one might expect. But exact calculations and measurements on this point will first be possible after accurate determination of the course of the vapour-tensions and electromotive forces.

The electromotive force between metals, however, increases with heating in the degree already given above, *i. e.* the calomel battery belongs, as I have already mentioned in the introduction to my first report, to the batteries which fix heat, which in part work at the expense of the thermometric heat of surrounding bodies.

A remarkable feature in these processes appears to me to consist in the fact that the attraction of the water to the salt to be dissolved can constitute so great a part of the chemical force acting between the oppositely propelled elements (zinc and mercury). In the existing measurements the electromotive force of the solution amounts in general only to about one eighth of the whole [electromotive] force of the concentrated solutions. But the electromotive force of the solution can yet be considerably increased by further dilution, in which state it no longer possesses sufficient constancy for exact measurements, and according to the formula given in equation (5 *a*) this electromotive force can be raised, with continually increasing values of *b*, to any degree we please. Thence it would follow that in very dilute solutions, or in acids wholly free from salt, traces of metals which we perhaps treat as unoxidizable in the acid considered may be able to be dissolved up to a certain limit with evolution of hydrogen. I note that quite similar relations must also hold for the solution of gases, in accordance with the mechanical theory of heat, whence views in some respects altogether changed as to the nature of galvanic polarization might be derived.

ON THE

THERMODYNAMICS

OF

CHEMICAL PROCESSES.

BY

PROFESSOR H. VON HELMHOLTZ.

PART III.

Zur Thermodynamik chemischer Vorgänge. Monats. der Berl. Akad. der Wissensch. May 31, 1883, pp. 647–665.

Deductions concerning Galvanic Polarization.

To the previous history of the law developed in my first communication "On the Thermodynamics of Chemical Processes," Feb. 2nd, 1882 *, I must now add that, as I have since learned, Lord Rayleigh, in a lecture delivered to the Royal Institution † on the 5th of March, 1875, laid down for the first time the general principle that the evolution of heat alone is not conclusive as to the possibility of a chemical change taking place in a given direction, but that change can occur only in those cases in which the Entropy (dissipation of energy) increases, or, at least, does not diminish.

That the development of heat taken by itself is not sufficient to determine the magnitude of the electromotive force of a galvanic element has been pointed out by F. Braun, in a series of papers beginning in 1878 [*], and demonstrated by him by means of a number of important experiments. The theoretical view, indeed, with which he sets out in the first of these papers—and specially the law that "Chemical Energy is of the nature of Heat," that every chemical process always gives rise in the first instance to heat, and that the proportion of the heat represented by the high temperature of the atoms first combined which is convertible into reversible work of other kinds is entirely a matter of accident,—is in my opinion opposed to facts, which show that galvanic batteries can do work even while they absorb heat. Such a process as Braun has imagined would not be reversible, and accordingly, if it went on during the solution of a metal, it could not proceed in the same way during the separation of the metal from solution. Since, moreover, Braun has recently expressed himself as agreeing with my analytical treatment of the principle, further discussion of this theoretical question is unnecessary.

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* [*Vid. supr.* p. 43.]

† [Proc. Roy. Inst. vii. p. 386.]

The great simplification produced in the thermodynamic laws by expressing the energy and entropy of a system as differential coefficients of an integral function was discovered, before me, by F. Massieu [†] in 1877, and completely expressed, at any rate for two variables, though without reference to chemical processes. He terms this integral function,—which he denotes by H, and which corresponds to my $-\mathfrak{F}$,—the "characteristic function of the body." I prefer to retain the name of "free energy," which I employed for the function $\mathfrak{F}$, since this name expresses more clearly the important physical significance of the quantity.

Massieu has expressed the law in a form somewhat more general and more advantageous for the convenient execution of certain calculations. In my deduction of the law the assumption is made that the parameter p which, in conjunction with the temperature θ, completely defines the state of the system, should be chosen in such a way as to make the external work produced depend only on dp, not at all on $d\theta$. In general the parameter can always be selected in accordance with this condition; but its selection may entail conditions difficult to realize and to compute from, so that it is more convenient to employ other parameters, such that, if these be maintained constant, temperature-change cannot go on without evolution of work. The corresponding changes in the general formulæ are easy of investigation. Massieu gives an example of this kind, in which he uses pressure and temperature as the parameters for gaseous and liquid substances.

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[*] Wied. *Ann.* Bd. v. p. 182, Bd. xvi. p. 561, Bd. xvii. p. 592.

[†] *Mém. des Sav. étrang.* t. xxii.; *Journ. de Phys.* vi. p. 216.

Finally, the thermodynamical conditions of molecular and chemical processes, in systems of bodies consisting of mixtures or compounds of any number of different substances, have been analytically developed by J. Willard Gibbs * in a very comprehensive and general manner. Massieu's "characteristic function" reappears here under the name of "Force-function for constant temperature." The general results of all these investigations naturally exhibit no important differences, in so far as they are simple deductions from the well-known principles of thermodynamics.

These deductions from thermodynamics are of specially high importance for the theory of galvanic polarization, since it is clear that the excess of the free energy of the mixed electrolytic gases above that of water depends to a great extent on the pressure, while the development of heat during their combination is nearly independent of it. So long as it was supposed that the electromotive force of polarization was to be deduced from the heat evolved (as I had myself done in my earlier papers), the electromotive force had to be looked upon as very nearly constant, which made certain phenomena of the polarization of a voltameter almost inexplicable. But if the electromotive force be deduced from the free energy, it is obviously variable in the highest degree according to the saturation with gas of the liquid layers which lie close to the electrodes; thus the explanation of a great part of the phenomena of polarization is modified, and most of what was before unintelligible is now made clear.

Since my attempts to explain the processes going on in

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* "On the Equilibrium of Heterogeneous Substances," Trans. Connecticut Acad. iii. pp. 108–248, 343–524; Sill. Journ. 1878, xvi. pp. 441–458.

galvanic polarization are scattered through a series of previous papers*, and some of them require modification to bring them into accord with new points of view, I will here recapitulate them in a connected form.

The fundamental assumptions from which I have always started are the Law of the Conservation of Energy and the rigid applicability of Faraday's Law of Electrolysis. In accordance with the latter I maintain that electricity can pass from the liquid to the electrodes only on the condition that an equivalent amount of chemical decomposition occur, and that unless the work necessary for the dissociation of the chemical compound can be supplied by the electric forces present this transfer cannot take place, but the bounding surface acts like a layer of perfectly insulating material.

If the two electrodes of a voltameter be charged, and maintained at different potentials, electric forces corresponding to the slope of potential act within the fluid, driving +E to the kathode, −E to the anode. This movement of electricity never takes place, so far as we know, without a simultaneous motion of the ions of the electrolyte, to which the +E and −E set in motion are attached. Positively charged hydrogen (H+.H+) passes therefore to the negatively charged kathode, and negatively charged oxygen (−O−) to the positively charged anode †. If, subsequently, evolution of gas takes place, the gases evolved are electrically neutral. Accordingly, if the principle of Faraday's law be consistently applied to this instance, the evolved hydrogen must be (H+.H−), and the liberated oxygen must be either (−O−.+O+) or (−O+). Since the molecule of evolved oxygen consists of either two or (ozone) three atoms, I consider the first form the more probable. Ozone would be (−O−.+O−.+O+).

The accumulation thus produced of (H+) at the negatively charged kathode, and of (−O−) at the positively charged anode is indicated by the "condensation current" which enters the electrodes while undergoing polarization. In this case the two electrode surfaces behave like two condenser plates of enormous capacity, owing to the extraordinarily small, *i. e.* only molecular, distance apart of the oppositely charged layers. If, after removing the battery, the two electrodes are joined by a simple conducting wire, the two condensers are discharged back through the wire, thus giving the "depolarizing current." To the electrical movement thus set up, which does not extend beyond the boundary of the liquid conductor, the chemical forces within the liquid appear to offer no resistance, since under the influence of electromotive forces, electrolytic conductors assume a condition of electrostatic equilibrium quite as completely as metals. This is proved to a high degree of accuracy by Sir W. Thomson's water-dropping collector, in which the weakest electromotive forces are able to charge the separating water-drops to a condition of perfect electrostatic equilibrium. In decomposing-cells freed as completely as possible from air I have myself succeeded in following out the proportionality between the electromotive force and the amount of condensed charge—a proportion easily demonstrated for very small electromotive forces—down to electromotive forces of 0·0001 Daniell. On the other hand, the transfer of electricity from the charged ions of the boundary-layer to the metal obviously takes place subject to the resistance of the chemical forces. It is the electrical discharging of the ions which definitively ruptures the chemical combination; so long as they are not discharged they can still return from the accumulated mass of atoms in the boundary-layer, and assume their previous state of combination, without any evolution of heat taking place, provided that the diminution in the electrical attractions which retain them at the electrodes be slow. This leads to the conclusion that the greatest and most essential part of chemical force, that namely which holds together really typical compounds, is based on the different attractions of elementary substances for the two electricities. Faraday's law compels us therefore to assume that each valency of every element is always charged with one whole equivalent either of positive or of negative electricity, and that the magnitude of these equivalents of electricity is independent of the nature of the substance to which they are attached, just as the atomic weights of the several elements are independent of the combinations into which they enter; just as if electricity were itself divided into atoms.

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* *Monatsb. d. Akad.* 1873, p. 587, 1877, p. 713, 1880, p. 285; also Pogg. *Ann.* vol. cl. pp. 483–495; Wied. *Ann.* vol. iii. pp. 201–216, vol. xi. pp. 737–759; Faraday Lecture, Journ. Chem. Soc. vol. xxxix. pp. 277–304, 1881.

† [Misprinted "kathode" in the original.]

That the electric forces which we have here to consider are not by any means too small to yield the great quantities of work evolved in chemical separations and recombinations is obvious, if the enormous amount of equivalents of electricity accumulated by this process be considered. My calculation, given in the Faraday Lecture, proves that if the +E attached to the atoms of 1 milligram. of water could be transferred without loss to a sphere, and the −E to another sphere at a distance of 1 kilometre, the two spheres would attract each other with a force equal to the weight of 26800 kilogrammes. It is precisely in consequence of the enormous magnitude of these atomic charges that the relatively weak forces of attraction, which one or two Daniell's cells can exert, are competent to produce so comparatively large an amount of work. These forces are weak only in relation to the small quantities of free electricity yielded by our electrical machines.

The formation of the electric double-layers necessary for the setting-up of electrical equilibrium explains a large and important part of the process going on in polarization, viz. the strong initial current during the charge and discharge of the electrodes. These currents can be made of sensibly greater duration if simultaneous occlusion * of one or both gases in the metal of the electrodes takes place. But neither of these two processes explains the unlimited duration of the current with feeble electromotive forces.

In my paper of the year 1873 I showed that the gases, especially atmospheric oxygen, dissolved in the liquid electrolyte, exert the very greatest influence on the strength of the continuous current, and I explained the origin of the currents depending thereon, viz. the convection-currents. In this case we have to bear in mind that electrically neutral gases dissolved

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* In my paper on "Currents due to Motion with Polarized Platinum' (Bewegungsströme am polarisirten Platina, *Monatsb. d. Akad.* 1880) I have over-estimated this influence, as I supposed the counter-electromotive force of the water-decomposition to be invariable. I now perceive that many of the explanations there given may be deduced much more simply and sequentially from the diffusion of the gases in the liquid.

in the liquid are not subject to the action of the charged electrodes in the same way as the charged ions before their discharge, but can diffuse freely through the liquid. If we now assume a stronger attraction on the part of oxygen for negative electricity, neutral oxygen in solution will be able to saturate itself with $-E$ at the negatively charged kathode without resistance, or may even [in doing so] contribute positive work towards the maintenance of the current, and may then either unite with $(H+.H+)$ or set out on a new migration towards the anode, while at the same time a molecule of $(-O-)$ becomes neutral at the anode. The whole work done by the battery consists then only in this, that neutral oxygen dissolved at the kathode * in a part of the liquid poor in oxygen disappears as such, takes up a negative charge and becomes a constituent of water, while at the anode the anion of water becomes neutral dissolved oxygen, but passes into a part of the liquid rich in oxygen. A stationary current is possible so long as the same quantity of dissolved oxygen is brought back by diffusion from the anode to the kathode, as is carried as anion by the current from the kathode to the anode.

Since the publication of the above-mentioned paper I have made numerous experiments with a view to a more complete removal of the last traces of dissolved gases than I could at that time obtain, but without better result. I removed the liquid electrolyte out of contact with the mercury of the mercury-pump employed, since it was impossible quite to shut out the suspicion that minute traces of dissolved mercury-salts might be formed. I endeavoured to expel the air from a cell, sealed by fusion, by means of the gas evolved during electrolysis, and to remove the latter by the action of a palladium plate charged with hydrogen, which might reduce the oxygen to water and occlude the hydrogen under the influence of the electric current. The water in the cell fell with a sharp click as in the water-hammer, but the continuous current was always manifested.

All that can be accomplished with such cells I have lately

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* [Throughout the remainder of this sentence the words "anode" and "kathode" are interchanged in the original.—E. F. J. L.]

succeeded in doing more simply with small cells of blown glass, united to the upper end of a barometer-tube. It is best to employ four platinum-wire electrodes, fused into the glass opposite each other in the form of a cross, two arms of which can be platinized. In this way two electrodes can be employed to develop any desired quantity of gas, and the other two for measuring the polarization. The lower reservoir of the barometer is formed of a two-necked bottle; the barometer-tube is fitted air-tight into one of these necks, the other encloses a short glass tube, through which liquids and mercury can be added or withdrawn by means of a pipette. This tube can also be connected with a water air-pump, so as to withdraw the air from the barometer-cell. If the enclosed liquid be now heated to 30° or 40° C., it gives out great volumes of steam, which drive out the last traces of air. While air is allowed to slowly re-enter the bottle the mercury in the barometer-tube rises to the height of the barometric column, diminished by the tension of aqueous vapour. To remove freshly-formed gas from this apparatus is always easy, and very complete expulsion can be effected by boiling.

Nevertheless we can always convince ourselves that a condition of the fluid, such that a galvanometer of sufficient sensitiveness would not show a continuous current for electromotive forces smaller than one Daniell, is not attainable. I have of late years employed one of Siemens' instruments with astatic "bell-shaped" magnets, for which, with the arrangement adopted, one scale-division corresponds to a current-strength of 10^{-9} ampere. Such a current, which can be detected with perfect certainty, would require 334 years to decompose 1 milligram. of water. If, therefore, only 1 cubic centim. (0·0005 milligram.) of detonating gas at 0° and 760 millim. mercury-pressure were dissolved in the water, its constituents would only need to migrate once in 36 days from the anode to the kathode in order to give the observed current.

In like manner it became evident that, even in cells freed as completely as possible from air, the polarization had not reached its highest limit when evolution of bubbles of gas commenced, and when therefore the electromotive force of the battery had become great enough to overcome the resistance of the chemical forces; on the contrary, the counter-electromotive force of polarization always increased with increasing electromotive force of the polarizing battery, even though a brisk evolution of gas had existed for a considerable time.

Finally, with all values of the electromotive force which lie near to the limiting value corresponding to evolution of gas, nothing is discoverable in the behaviour of the current which points to a sudden overpowering of the chemical by the electromotive forces.

The thermodynamical theory now offers a satisfactory way out of these difficulties, since it shows that, if the gases formed be dissolved in the liquid electrolyte, the resistance due to the chemical forces, which the current has to overcome, must become continually greater and greater as more of the evolved gas enters into solution round about the electrodes, and that the part contributed by the gas to this resistance is by no means inconsiderable, but may attain any conceivable positive value between 0 and ∞.

That the decomposition of water under high pressure may cease even with electromotive forces of 3 or 4 Daniells has been shown by Werner Siemens[*]. Unfortunately we have no statement of the magnitude of the pressure attained and of the strength of the convection-currents set up at the same time, although this must considerably diminish the portion of the electromotive force available for the production of chemical work.

Thermodynamical Calculation of the Free Energy of Detonating Gas.

I denote by U_g the total internal energy for 1 grm. of detonating gas, in the case in which the two gases are supposed not to be mixed together[†]. U_g is a function of the temperature and of the densities of the two gases, which three quantities form the independent variables of the problem. U_w is the total internal energy of 1 grm. of water at the same absolute temperature θ for which U_g is determined. Then $(U_g - U_w)$ is the mechanical equivalent of the heat developed during the combustion of the detonating gas and its conversion into liquid water. It must, however, be noted that, if the gas be at atmospheric pressure before and during the combustion, an additional quantity of heat will be developed by this pressure, since the volume of the gas diminishes to that of the water formed. The latter quantity of heat is

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[*] *Gesammelte Abhandlungen und Vorträge*, p. 445.

[†] Mixing them would alter the free energy, as Lord Rayleigh has shown (Phil. Mag. April 1875). *Vide* also L. Boltzmann, *Sitzb. der k. Akad. der Wissensch. zu Wien*, Bd. lxxviii. Abth. ii. (Oct. 10, 1878).

$$Q = \frac{p \cdot v}{\mathfrak{J}},$$

if p denote the normal atmospheric pressure, v the volume of 1 grm. of detonating gas under pressure p, and $\mathfrak{J}$ the mechanical equivalent of heat.

Within limits of temperature such that the specific heats of water and the gases do not vary sensibly, the heat evolved must be of the form

$$U_g - U_w = C - \mathfrak{J} . \mathfrak{k} . \theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\mathfrak{k} = 1 - \frac{2\alpha_h \gamma_h + \alpha_o \gamma_o}{2\alpha_h + \alpha_o},$$

where α_h and α_o denote the atomic weights of hydrogen and oxygen, γ_h and γ_o their specific heats at constant volume. If the gases be kept at constant volume, and if we neglect the mechanical work evolved by the small changes in volume of the water, there only remains to be considered, in the case of rise of temperature, the change of the internal energy effected by the absorption of heat.

Moreover, changes of volume of the gas have no marked influence on the value of U, since both gases very nearly fulfil the conditions of a perfect gas; hence the external work is the exact equivalent of the heat which disappears, and accordingly the change in the value of U is compensated by restoring the previous temperature. The numerical values in the above formula come out as follows:—Denoting by v the volume of 1 grm. of gas under pressure p and temperature θ, and putting

$$\frac{p \cdot v}{\theta} = R, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

denoting further the specific heat at constant pressure by c, we have

$$\alpha_h = 1 ; \quad \alpha_o = 16.$$

$$\mathfrak{J}.\gamma_h = \mathfrak{J}.c_h - R_h ; \quad \mathfrak{J}.\gamma_o = \mathfrak{J}.c_o - R_o.$$

According to Regnault,

$$c_h = 3{\cdot}4090$$
$$c_o = 0{\cdot}2175$$
$$v_h = 11163{\cdot}6 \frac{cm^3}{g} \text{ for } 0° \text{ and } 760 \text{ mm.}$$

Hence

$$\gamma_h = 2{\cdot}29965$$
$$\gamma_o = 0{\cdot}17371$$
$$\mathfrak{k} = 0{\cdot}58007^*.$$

From Schuller and Wartha's† experiments with an ice-calorimeter, the mean value 34123·56 calories was obtained for the heat developed by the combustion of 1 grm. of hydrogen to form liquid water, and therefore 3791·5 calories were developed in the formation of 1 grm. of water. Of this the work done by the atmospheric pressure contributed 45·232 calories; there remain 3746·268 for the work done at 0° by chemical processes. Hence we obtain for the constant C of equation (1),

$$C = \mathfrak{J} \times 3904{\cdot}63.$$

Employing the notation of my former communication‡, the total energy of a system of bodies may be deduced from the free energy by means of the following relation §:

$$U = \mathfrak{F} - \theta . \frac{\mathfrak{F}}{\partial\theta},$$

or

$$-\frac{U}{\theta^2} = \frac{\partial}{\partial\theta} . \left(\frac{\mathfrak{F}}{\theta}\right).$$

Substituting in this equation the value of $U_g - U_w$ from equation (1) and integrating, we obtain

$$\mathfrak{F}_g - \mathfrak{F}_w = C + \mathfrak{J}.\mathfrak{k}.\theta.\log\theta + \theta.\phi, \quad . \quad . \quad . \quad . \quad (1{\cdot}b)$$

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* [These values do not agree with the data which, taking $\mathfrak{J} = 423{\cdot}7$ (metre-grammes), give $\gamma_h = 2{\cdot}4022$, $\gamma_o = 0{\cdot}1552$, $\mathfrak{k} = 0{\cdot}5951$. With this value of $\mathfrak{k}$, C becomes $\mathfrak{J} \times 3908{\cdot}63$; the value given in the text for $\mathfrak{k}$ makes $C = \mathfrak{J} \times 3904{\cdot}8$, or nearly as printed.]

† Wied. *Ann.* ii. p. 378: value (α).

‡ [*Vid. supr.* p. 43.]

§ [See above p. 53, eq. (1 *h*).]

where ϕ is the constant of integration, which is independent of θ, but may depend on v_h and v_o. Its dependence on the two last-mentioned quantities is shown if we determine the work done by change of volume of the separate gases. The integral $\mathfrak{F}_g$ is alone dependent on both these quantities :

$$\frac{\partial \mathfrak{F}_g}{\partial v_h} = - \frac{2p_h . \alpha_h}{2\alpha + \alpha_o}; \quad \frac{\partial \mathfrak{F}_g}{\partial v_o} = - \frac{p_o \alpha_o}{2\alpha_h + \alpha_o}.$$

Employing equation (1 *a*) we obtain

$$\frac{\partial \mathfrak{F}_g}{\partial v_h} = - \mathrm{R}_h . \frac{\theta}{v_h} . \frac{2\alpha_h}{2\alpha_h + \alpha_o};$$

and

$$\frac{\partial \mathfrak{F}_g}{\partial v_o} = - \mathrm{R}_o . \frac{\theta}{v_o} . \frac{\alpha_o}{2\alpha_h + \alpha_o}.$$

By equation (1 *b*), however,

$$\frac{\partial \mathfrak{F}_g}{\partial v_h} = \theta . \frac{\partial \phi}{\partial v_h}; \text{ and } \frac{\partial \mathfrak{F}_g}{\partial v_o} = \theta . \frac{\partial \phi}{\partial v_o}.$$

Therefore

$$\phi = - \mathrm{R}_h . \frac{2\alpha_h}{2\alpha_h + \alpha_o} \log v_h - \mathrm{R}_o . \frac{\alpha_o}{2\alpha_h + \alpha_o} . \log v_o + \mathrm{H}', . \quad (1\, c)^*$$

where H′ denotes a constant of integration.

The whole additional amount of free energy possessed by the separated gases, beyond what is possessed by water, thus comes to be

$$\mathfrak{F}_g - \mathfrak{F}_w = \mathrm{C} + \mathfrak{J} . \mathfrak{f} . \theta . \log \left(\frac{\theta}{\theta_0}\right) - \theta . \left[\frac{\mathrm{R}_h . 2\alpha_h}{2\alpha_h + \alpha_o} \log (v_h) + \frac{\mathrm{R}_o \alpha_o}{2\alpha_h + \alpha_o} \log (v_o) + \mathrm{H}\right], . \quad (1\, c)$$

where $\mathrm{H} = \mathrm{H}' + \mathfrak{J} . \mathfrak{f} . \log (\theta_0)$

only corresponds to another way of writing the constant of integration, and θ_0 denotes any suitably chosen normal temperature,—that of melting ice, for example.

It must further be remarked that for perfect gases we must have, in accordance with Avogadro's law,

$$\mathrm{R}_h . \alpha_h = \mathrm{R}_o . \alpha_o. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1\, d)$$

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* [So marked in orig.; apparently a misprint.]

Equation (1 *c*) shows that the work to be obtained from the combination of gases depends certainly, and in a very essential manner, on their densities before combination, while this is not the case with the heat evolved during the combination, provided that external sources of work, such as the pressure of the atmosphere, do not interfere. Since the volumes v_h and v_o may assume all positive values from 0 to ∞, their logarithms may have any value between $-\infty$ and $+\infty$; and since the remaining quantities on the right-hand side of the equation are all necessarily finite, the value of $\mathfrak{F}_g - \mathfrak{F}_w$ may extend from $-\infty$ to $+\infty$, or at least, seeing that negative values exclude the possibility of combustion, from 0 to $+\infty$.

Work-equivalent of Dissolved Gases.

During electrolytic decomposition the gases are at first dissolved in the liquid electrolyte, and then, if the amount dissolved in the bounding-layer in contact with the electrodes exceed the limits of saturation which can exist under the given pressure, they are evolved in bubbles.

If a gas be dissolved to saturation in a volume V of water under pressure *p*, the amount dissolved is given by the equation

$$\frac{bp}{\theta} = \mathrm{R} . \frac{m}{\mathrm{V}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where *b* is Bunsen's "coefficient of absorption," a quantity which is itself a function of the temperature.

If an amount *dm* leave the liquid, there is produced as the first part of the work

$$-d\mathfrak{F}_1 = p . v . dm.$$

Next, let the evolved gas be brought to a standard condition, which we may denote by the suffix 1, then we obtain for the second part of the work

$$d\mathfrak{F}_2 = dm . \int_v^{v_1} p . dv$$

$$= dm . p_1 . v_1 - dm \int_p^{p_1} v . dp - dm . p . v.$$

Accordingly the total work, produced by the evolution of the mass of gas dm from the fluid and its reduction to the standard state, is

$$\left.\begin{aligned} -d\mathfrak{F} &= -(d\mathfrak{F}_1 + d\mathfrak{F}_2) \\ &= \theta.\mathrm{R}.dm\left[1 - \log\left(\frac{p_1}{p}\right)\right] \\ &= \theta.\mathrm{R}.dm\left[1 + \log\left(\frac{v_1}{v}\right)\right] \\ &= \theta.\mathrm{R}.dm\left[1 - \log\left(\frac{m_1}{m}\right)\right] \end{aligned}\right\} \quad \ldots\ldots \quad (2a)$$

In the last equation m_1 denotes the quantity of gas which would be dissolved under the pressure p_1, corresponding to the standard state.

These equations show that, with diminishing values of m, an increasing supply of work is required in order to take away equal amounts dm from the liquid; and therefore that the fluid adheres to, or attracts, the last portions of dissolved gas with a force which increases without limit.

If therefore, during the decomposition of water, the elements set free are not evolved as gases under pressure p_1, but remain dissolved in the liquid, then $d\mathfrak{F}$ calculated for one gramme of explosive gas must be subtracted, as not having been performed, from the work required for the decomposition of water. This gives therefore for 1 grm. of water,

$$\mathfrak{F}_g - \mathfrak{F}_w = \mathrm{C} + \mathfrak{J}.\mathfrak{f}.\theta.\log\frac{\theta}{\theta_0}$$

$$+\,\theta\left\{\mathrm{R}_h.\frac{2\alpha_h}{2\alpha_h + \alpha_o}(1 - \log v_h) + \mathrm{R}_o.\frac{\alpha_o}{2\alpha_h + \alpha_o}.(1 - \log v_o) - \mathrm{H}\right\} \quad (3)$$

Here v_h and v_o denote the specific volumes which the gases lying above the liquid must possess in order to bring about the same degree of saturation as the gas dissolved in the bounding-layers at the electrodes has produced. In this case, therefore, if very little gas be dissolved, and the corresponding values of v are therefore very great, the quantity $(\mathfrak{F}_g - \mathfrak{F}_w)$ may be zero, or even negative. Stable equilibrium among the chemical forces of water is accordingly possible only for a certain minimum amount of dissociation of its elements, and, on the other hand, the less the amount of the gases considered which is dissolved in the water, the smaller is the expenditure of work—by an external source of electromotive force employed for the purpose—needed to bring about further decomposition. Strictly speaking, therefore, a convection-current through an aqueous electrolyte can never be quite absent even with the feeblest electromotive forces; while with stronger electromotive forces the amount of dissolved gases must be increased, and with it the convection-current. On the other hand, the slowness of the process of diffusion explains why it is that many days may elapse before the stationary condition of solution of gas and of the current is set up under the action of a constant electromotive force. It is hence further made clear that every motion of the liquid, whether set up by mechanical causes or by inequalities of temperature, must produce a change—in general an augmentation—of the current-strength, since it disturbs the arrangement of fluid layers of different gas-content. These two circumstances render the carrying out of investigations on the stationary condition very difficult, since such experiments require a very long time, and disturbance by shaking can scarcely be avoided, at any rate in the centre of a large town. Galvanic batteries of sufficient constancy may be very well made up from calomel elements or other similar combinations, since the strength of the currents required is but small. In my last series of experiments, however, I took care to employ elements of this description, always compensated and therefore nearly free from current, for measuring the electromotive forces employed, and to determine from time to time the electromotive forces of those which had to furnish continuous currents by comparison with that of cells through which no current was allowed to pass.

Employing the ohm, the volt, and the ampere as our units, $A\,J\,t = J^2 W\,t$ is the work done in time t by the electromotive force A when J is the current, expressed in terms of the units centigram. $\times 10^{-9}$, centim. $\times 10^{9}$, and second. The unit of work is the watt, as defined by Sir William Siemens, which is ten million times greater than the unit of work of the C.G.S. system, upon which we have based our estimate of the work done by a gas.

If we denote by η the quantity of water decomposed by

1 ampere in a second (according to F. Kohlrausch* $\eta = 0{\cdot}00009476$), we obtain for the work done per second by 1 ampere in decomposing water

$$A = 10^{-7} . \eta . (\mathfrak{F}_g - \mathfrak{F}_w) . \quad . \quad . \quad . \quad . \qquad (3\,a)$$

If we substitute the value of the quantity in brackets from equation (3), and denote by A_a the electromotive force set up if the evolved gases be at an atmospheric pressure p_a, then

$$v_h = R_h . \frac{\theta}{p_a}, \qquad \text{and} \qquad v_o = R_o . \frac{\theta}{p_a};$$

therefore

$$\left.\begin{aligned} A_a = 10^{-7} . \eta . \Big[C + \mathfrak{J} . \mathfrak{f}_a . \theta . \log\left(\frac{\theta}{\theta_0}\right) + \theta . \Big\{ R_h . \frac{2\alpha_h}{2\alpha_h + \alpha_o} . \log(p_a) \\ + R_o . \frac{\alpha}{2\alpha_h + \alpha_o} . \log(p_a) - H_a \Big\} \Big] \\ \mathfrak{f} = \frac{2\alpha_h(1-c_h) + \alpha_o(1-c_o)}{2\alpha_h + \alpha_o} = 0{\cdot}5970\dagger \qquad \qquad \qquad \\ H_a = H + \mathfrak{J} . \mathfrak{f}_a . \log \theta_0 - R_h . \frac{2\alpha_h}{2\alpha_h + \alpha_o} (1 - \log R_h) \\ - R_o . \frac{\alpha_o}{2\alpha_h + \alpha_o} (1 - \log R_o) \end{aligned}\right\} (3\,b)$$

Accordingly for any other value of the pressure of the dissolved gases,

$$A = A_a + 10^{-7} . \eta . \theta \Big\{ R_h . \frac{2\alpha_h}{2\alpha_h + \alpha_o} . \log\left(\frac{p_h}{p_a}\right) \\ + R_o . \frac{\alpha_o}{2\alpha_h + \alpha_o} . \log\left(\frac{p_o}{p_a}\right) \Big\} . \quad . \qquad (3\,c)$$

In order to give an approximate estimate of the degree of variability of the electromotive force, I will use for the value of A_a the value of the electromotive force obtained on the first appearance of gas-bubbles in the barometer-cells; hence

$$A_a = 1{\cdot}6447 \text{ volt.}$$

If detonating gas be only dissolved in the liquid, and if $\mathfrak{p}$

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* Pogg. *Ann.* Bd. cxlix. p. 175. It is there given in mgrm. for 1 weber.

† [c_h and c_o in this formula should be γ_h and γ_o, according to the notation given on page 85. The numerical value of $\mathfrak{f}$ should be 0·5951.—See footnote on p. 86.]

denote the pressure which the evolved gas would exert if it occupied a volume equal to that of the liquid, then

$$\tfrac{2}{3}\,.\,\mathfrak{p}=b_h\,.\,p_h, \quad \text{and} \quad \tfrac{1}{3}\,.\,\mathfrak{p}=b_o\,.\,p_o. \quad . \quad . \quad (3\,d)$$

The absorption coefficients (b) at 20° C. are, according to R. Bunsen,

$$b_h=0{\cdot}0193,$$
$$b\ =0{\cdot}0480.$$

With these data, equation ($2\,b$) gives for $A=0$,

$$\mathfrak{p}=\frac{p_a}{3{\cdot}420\times10^{38}}=p_a\times0{\cdot}2923\times10^{-38},$$

or $0{\cdot}2655\times10^{-36}$ gramme of detonating gas per cubic centim. of liquid, while with the best mercury-pumps a vacuum of only about $p_a\,.\,10^{-8}$ has been attained *. In all chemical and even galvanic investigations such a quantity must be treated as insensible.

The difference (A_a-A) must therefore be reduced, by the setting up of an electromotive force A and increasing it, to about one fourth of A_a (accordingly $A=1{\cdot}2$ volt, or about 1 Daniell) before the dissolved gas begins to be perceptible.

If $\mathfrak{p}$ be chosen so as to correspond to the amount of decomposition effected per second by a current of one scale-division of my galvanometer, and if the evolved gas be supposed to be concentrated into one cubic centim. of the liquid, then

$$\mathfrak{p}=\frac{\eta\,.\,10^{-9}}{v_h},$$

whence, by means of equations ($3\,c$) and ($3\,d$), we obtain the values

$$A_a-A=0{\cdot}33745,$$
$$A=1{\cdot}3 \text{ volt.}$$

Since my barometer-cell contained about 100 cubic centim. of water, which, if the current be stationary, must on an average receive half as strong a charge of gas as was assumed, the dissociation-current could produce in this case a deviation of 1 scale-division for 50 seconds. We may consider this as about the limit of what can be detected galvanometrically.

If, however, the whole electromotive force A_a be present,

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* E. Bessel Hagen, Wied. *Ann.* Bd. xii. p. 438.

the quantity in brackets on the right-hand side of equation (3 *c*) will vanish, *i. e.*

$$\frac{\mathfrak{p}}{p_a}=0{\cdot}04942,$$

which corresponds to a current the time-integral of which for 100 cubic centim. of liquid amounts to 2176 millions of scale-divisions multiplied by a second.

My investigations, communicated March 11, 1880 *, actually showed currents which were continuous, and of strikingly greater strength if the electromotive force was increased somewhat beyond the limiting value of 1 Daniell than was the case with smaller electromotive forces; and the same phenomenon has been uniformly exhibited in my later researches. In order to be able merely to observe this stronger current at the limit of gas-evolution, I find it necessary to diminish very considerably the fraction of the current which goes through the galvanometer, *i. e.* to about $\frac{1}{630}$. The strength of the convection-current still present is about 0·001 ampere. But even if this current were entirely employed in the evolution of gas, 36 minutes would have to elapse before the quantity of gas needed to saturate the liquid would be evolved. In reality several hours, or even days, are required, since the greatest part of the current under discussion corresponds not to the evolution of gas, but merely to the diffusion of gas already evolved.

The temperature-coefficient of the electromotive force A_a is shown by the above formulæ to have a very small value. viz. about $\frac{1}{3000}$ part of its value for 1° C.

Formation of Bubbles of Gas.

If the layers of liquid against the electrodes have become sufficiently saturated with gas to allow of the formation of bubbles of gas under the pressure exerted on the liquid, these will begin to ascend. The bubbles contain only the gas separated at one of the electrodes, together with the amount of aqueous vapour corresponding to the temperature. They are subject to the pressure of the mass of gas lying above the liquid, to that of the superincumbent water-column, and lastly to the capillary tension of the spherical boundary of the surrounding water. The pressure within a spherical capillary surface is, as is well known,

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* *Wissensch. Abh.* Bd. i. p. 903.

$$p=\frac{2T}{r},$$

if r be the radius of the sphere and T the surface-tension. If we put the latter, in accordance with G. Quincke's determinations, equal to the weight of 8·253 milligram. per millim., then in a bubble of 0·1 millim. radius the pressure p is that of 12·14 millim. of mercury, and in very small bubbles of 0·01 millim. radius ten times as much. It is thus clear that the first formation of the escaping bubbles is attended with considerable difficulty, a fact which, as is well known, presents itself in a very striking manner in the retarded ebullition of liquids free from air. In general the formation of bubbles appears to take place most easily at the surface of contact between the liquid and a solid boundary for which it has no great adhesion. How great the influence of the boundary may be in this case is well known from the study of retardation of boiling. Carbonic acid dissolved in water is evolved much more freely from metals, especially the noble metals, than from glass, and better from roughened or sharp-edged pieces of glass than from pieces entirely smooth. Electrolytic gases behave in a similar way. A higher initial electromotive force has to be employed, in order to produce the first few bubbles, than is needed afterwards to keep up the evolution of gas. When this has once begun we may descend by small degrees to feebler electromotive forces. The bubbles in that case begin finally to rise only from one or a few points on the wire. If the evolution of gas be stopped, even for a few minutes, by a too great or too rapid weakening of the electromotive force, a much greater force must again be resorted to in order to set up a fresh stream of bubbles. Obviously the rift between the liquid and electrode has been filled up and must be formed afresh.

Accordingly the initial evolution of gas may depend on many small accidents occurring at the surface of the electrodes. Platinum forms bubbles more easily when platinized than when smooth.

The evolution of gas must exert an essential influence upon the counter electromotive force of the voltameter, *i. e.* upon the quantity commonly styled the "intensity of polarization," inasmuch as the chemical work depends, according to the theory given above, on the gaseous charging of the boundary-layers of liquid, which will be diminished by the evolution of gas. In this fact may lie the explanation of the varying electromotive force of one-fluid galvanic elements, in which hydrogen is evolved against various metals. When the bubbles are formed with difficulty, the hydrogen must of necessity be separated within a liquid strongly saturated with this gas, and this requires a larger amount of free energy. This may be the case with base metals opposed to platinum, and may explain their varying behaviour. These circumstances accordingly increase in a very high degree the difficulty of measuring the electromotive force required in any given case in order to set up a continuous evolution of gas; and, indeed, the hindrance to the formation of bubbles becomes relatively much greater in those cases in which the liquid contains smaller quantities of gas, since in these cases it will be more difficult to collect the gas together at one point, which is necessary in order to keep in equilibrium the tension of the capillary surface, which tension remains uniform if the size of the bubbles be uniform. For this purpose, with equally large bubbles the same amount of gas must always be furnished, while the quantity which supports the pressure of the atmosphere above the liquid is proportional to this pressure, so that less gas is required for the filling of the bubbles in proportion as the liquid contains less.

As a matter of fact I found that, if the abstraction of gas from above the liquid were as complete as possible, bubbles were evolved under a lower electromotive force than if the pressure of the detonating gas above the liquid reached $\frac{1}{3}$ or $\frac{1}{2}$ of an atmosphere. The differences, however, were not as great as might be expected from theory. I have seen bubbles formed under 1·5877 volts when the pressure above the liquid was only that of its own vapour, without measurable gas-pressure; while in the same vessel the formation of gas bubbles first took place under 1·6314 volts, when a pressure of 380 millim. of mercury from detonating gas and 16 millim.

from water-vapour was exerted on the fluid. Moreover, I have convinced myself that, with electromotive forces even smaller than those given at first, the barometer falls slowly, although no further visible evolution of gas occurs ; and I hope by determining the limit of its fall to obtain a more exact measure of the electromotive force corresponding to a determinate pressure, than the observation of bubble-formation has already afforded me. Such investigations require, however, a comparatively long time ; I am unable, therefore, at present to present them in a complete form.

Work done during Diffusion.

If a quantity δm of a dissolved gas pass from a more saturated part of the fluid containing $m+dm$ in unit volume to another less saturated part containing only m, a quantity of free energy disappears, the amount of which according to equation (2 *a*) would be

$$\frac{\partial}{\partial m}\,.\,\delta\mathfrak{F}=\frac{\theta\,.\,\mathrm{R}}{m}\,.\,\delta m. \qquad . \quad . \quad . \quad . \quad . \qquad (4)$$

This work-equivalent can be transformed only into heat, since no other form of free energy is reproduced therefrom. To the development of heat by the current, corresponding to the friction of the electrolytically transported ions in the electrolyte, must therefore be added the heat developed in the same liquid by the diffusion of the dissolved electrically neutral components, which migrate in the opposite direction to the ions of the same kind. If we designate as " resistance " every process which changes a part of the energy of the electric current into heat, a process is thus obtained which may be termed the " transfer resistance of the cell."

If the transition assumed above from the state of saturation $m+dm$ to m take place in an element of length ds, then the value of the corresponding amount of work given above divided by ds is the force tending to propel each element of the mass dm in the direction of ds. Since this force is directly, while the mass propelled is inversely, proportional to m, the velocity of diffusion must be independent of m and proportional to $\frac{\partial m}{\partial s}$, within such limiting values of the densities of the dissolved gases that the friction between the diffusing mass and the water is independent of its density and proportional to its velocity. Thence we obtain for each gas, within the limits in which the said conditions hold, by analogy with the well-known theory of the conduction of heat,

$$\frac{\partial m}{\partial t} = -k^2 \left\{ \frac{\partial^2 m}{\partial x^2} + \frac{\partial^2 m}{\partial y^2} + \frac{\partial^2 m}{\partial z^2} \right\}, \quad . \quad . \quad . \quad . \quad (5)$$

in which m, as defined above, denotes the quantity of gas dissolved in unit volume, and k^2 is a constant depending on the nature of the gas and the liquid.

Equation (5), the form of the integration of which is known from the theory of the conduction of heat, combined with those set forth previously, allows us to give, at least for an electrolytic conductor of prismatic form, a tolerably complete analytical theory of polarization-currents, the deductions from which appear to agree with the phenomena in all essential particulars.

FURTHER RESEARCHES

RESPECTING THE

ELECTROLYSIS OF WATER.

BY

PROFESSOR H. VON HELMHOLTZ.

Weitere Untersuchungen, die Elektrolyse des Wassers betreffend. Sitzungsbericht der Akademie der Wissenschaften zu Berlin, 1887, pp. 749–757.

On the 10th May, 1883, I laid before the Berlin Academy a series of thermodynamic laws having reference to the decomposition of water by galvanic currents. These led to the result, important for the doctrine of polarization, that electrolytic decomposition of water can be brought about by electromotive forces which may be smaller the smaller the quantities of hydrogen and oxygen that exist dissolved in the neighbourhood of the electrodes; so that in fact no other limit than zero can be assigned for the smallest electromotive force capable of decomposing water that is perfectly free from gas. At the same time it was to be remarked that the quantities of explosive gas evolved for [electromotive] forces which amount to less than 1·5 volt are so extraordinarily small that they can be perceived in no other way than by the weak residual currents which they maintain. Moreover, I have on the former occasion already demonstrated that in water which originally was completely free from gases, even the weakest electromotive force is capable of maintaining a permanent electric current through the liquid. For the smallest quantity of the gas which at the electrodes has become free and electrically neutral, will penetrate little by little, by the process of diffusion, to the opposite electrode, and thereby will set free a fresh quantity of a polarizing current in the direction of the battery-current. To be sure, chemically recognizable quantities of dissolved oxygen and hydrogen must act incomparably more strongly.

I have since then taken much trouble to establish experimentally the limits for the minimum electromotive forces which are competent to develop fresh gas under a given pressure of the mixed gas upon the liquid. The investigations require usually a very long time, and I cannot yet regard them as completed in every direction. Meanwhile I can at least give the methods by which the above-mentioned variability of the electromotive force may be proved.

Respecting the measurements to be here brought forward on the electromotive force of decomposition of water, I must first draw attention to a source of error which has not been sufficiently considered by previous observers, and only partially so in my own earlier investigations, and which may considerably vitiate the results of researches that only last a short time. Namely, that if an anode of platinum or both electrodes contain occluded hydrogen or combustible gases in general, so that the oxygen evolved by the current can combine with the gases at the anode, then a much smaller electromotive force will be able to liberate hydrogen at the kathode. This is especially the case if the kathode is small and the anode large. In such researches all platinum which has been cleaned by ignition in flame appears to contain combustible gases from the interior of the flame. The same action is produced if a previous current in the opposite direction has left behind a store of hydrogen in the film of water adhering to what is now the anode.

This cause of the development of gas is to be recognized by the fact that it does not last long, and mostly diminishes rapidly in strength if one is careful to have a battery of constant electromotive force. But it may endure for days before the limit is reached when all active traces of the occluded hydrogen have disappeared. In the researches to be described, which mostly lasted for weeks and months, care was therefore taken to keep the current always in the same direction between the electrodes, when there arose no special grounds for altering it.

A further difficulty in researches of this nature lies in the fact that exactly the same impediment opposes the evolution of the dissolved gases in bubbles as besets the formation of the first bubbles of steam in retarded boiling. In liquids which contain very small amounts of gas these obstructions may be very considerable. For a long time I thought that I should best be able to determine the limit of decomposition of water in an air-freed column of liquid, which should be held up in the upper part of a barometer-tube by the cohesion of the liquid alone. Consider a siphon-barometer, the shorter limb of which can be closed by a glass tap and having a platinum wire sealed in through the upper curved top of the longer limb. Let it be filled with water slightly acidulated with sulphuric acid, and with the requisite quantity of quicksilver. Let the water ascend to the upper end of the long limb, set the barometer upright, whilst at the same time the tap is opened. The vacuum forms above, and the superfluous quicksilver flows away through the tap, which afterwards is closed. Now rinse out the whole closed tube with the vacuum, and let the water again ascend to the upper part of the long limb, but the air-bubbles to that of the short limb. This can be successfully done by holding the barometer almost level, but with the short limb higher than the long one. Then it is again turned upright; a new vacuum is formed by opening the tap; and the process is repeated again and again; whilst for the later stages one has recourse to warming the whole tube to about 40° C. In this way it is possible to expel the air more and more completely, until at last, on again laying down the tube, the newly-formed vacuum contracts to a minute air-bubble of only about 0·2 millim. diam.

When matters have been carried thus far, let the tube lie in an almost horizontal position, with the tap open, and let it cool down. After half an hour or a hour the little air-bubble is found to have been absorbed back into the liquid. One can then carefully turn the tube upright without the quicksilver sinking. It is held up by the adhesion of the water to the upper curved end of the glass, in spite of the rough platinum wire present at this point, also by the cohesion of the water, the adhesion of the quicksilver to the water, and the cohesion of the quicksilver. The negative pressure in the water from this cause amounted to about from 8 to 10 centims. of quicksilver. So far these phenomena had been already long known. But it is new, as I think, that one can join the opened end of the short limb, by means of a tube, to an air-pump and remove the whole atmospheric pressure without detaching the liquid*.

Through the suspended liquid an electric current may then be sent from the platinum to the quicksilver, evolving oxygen against the former, hydrogen against the latter. By increasing the electromotive force little by little the limit is at last reached where the column of liquid breaks away. The currents which I have used for this purpose were those given by the calomel-cell, which I have described † on a previous occasion. Since the water-decomposing currents which are thereby created are, after the polarization has fully set in, excessively feeble, these cells amply suffice for the purpose, and by applying such cells with different degrees of concentration of the zinc-chloride solution, and in combination with a weaker cell which contains cadmium ‡ instead of zinc, one may procure the most varied gradations of electromotive force and keep these unchanged for weeks together.

However, I obtained by this arrangement notably high and varied electromotive forces, going up to two volts, whilst I had already in earlier cases observed decomposition of water with much smaller forces. We shall find the same confirmed also in the final researches. But this method is specially adapted to show how great the resistance to the first formation of bubbles may become.

Some other different decomposition-cells, which, provided with two platinum electrodes, were fixed at the upper end of a barometer-tube, were examined under various degrees of exhaustion of the air. In the case of these it was regularly shown that when the electromotive force of the battery was slowly weakened the gas-bubbles were evolved only at solitary places on the platinum wires, and, finally, at only one particular spot, which remained unchanged for days together. But when, on a still further weakening of the electromotive force, the evolution of gas had ceased for even a few minutes only, then, on restoring the electromotive force to the same value which previously had caused gas-bubbles to rise, the evolution of gas was not again resumed. One was obliged to go back to considerably higher values before new bubbles formed. Then one could slowly descend again to the former degree. This could not be done quickly. The counter-electromotive force determined by the stronger accumulation of hydrogen must have time to diminish (which could only happen slowly by the diffusion of the hydrogen), or else the evolution of gas was arrested, and in consequence ceased again entirely.

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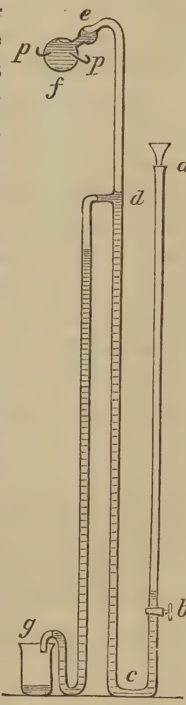
* I showed this experiment in my lectures both the last two winters, and also to the Physical Society [of Berlin] at its meeting on February 4, 1887.

† [*Vid. supr.* p. 64.]

‡ [According to Czapski (Wiedemann's *Annalen*, xxi. p. 235), the cadmium-cadmic-chloride-calomel-mercury cell has an E.M.F. of 0·7541 volt.—S. P. T.]

These experiments show clearly how little we can count upon being able to recognize the limits of decomposition of water by the ascent of the bubbles of gas.

I consequently entered upon another way, which finally led me to the following method. The decomposition of water is carried on in a cell at the upper end of a barometer, which has a side tube which can, like the Sprengel mercury-pump, continually remove the gas that collects. The apparatus for this is depicted in the annexed figure about a thirteenth of the real size. In it *a c d* is a barometer-tube, the open limb of which can be closed at *b* by a glass tap; *d g* is a narrow side-tube (of 2 millims. internal diameter), which serves as a mercury pump. At *e* and *f* is the decomposing-cell, con-



sisting of two glass bulbs. The upper one *e* is the smaller; the lower, larger one has two platinum wires *p p* as electrodes. One first fills up the bulbs with water acidulated with one per cent. of sulphuric acid, then sets the apparatus upright, and pours quicksilver in through the funnel at *a*. As soon as the quicksilver has ascended in both limbs to the height of the opening *d*, it begins to flow down through the tube *dg* and takes the air away out of the space *de*. At the same time the air dissolved in the water is evolved in bubbles which become little by little more infrequent and bigger, and which eject the superfluous water, so that it also flows away down the tube *dg*. Since by this action the tube becomes wetted, and since also at a later stage the water-vapour that is sucked over condenses in this part, this tube must be proportionately narrow in order that the drops of mercury, in spite of the diminished capillary tension of their wet surfaces, may not easily permit the liquid and the air that is imprisoned between them to ascend again. At high degrees of the exhaustion the very minute little bubbles usually do climb up many times, until several of them have united together into one large bubble which can no longer break through the quicksilver, and which is ejected. Into the upper space they cannot return; for it is only at the moments when a rapid downflow begins that the mercury-seal at *d* opens at the newly-formed gaps in the flowing thread of quicksilver; and at the end of the downwardly directed movement of the thread, when the ascent of single air-bubbles and water-drops begins, it is again closed.

I had from previous experience long doubted whether a Sprengel pump would work when wet internally, but with a sufficiently narrow tube it goes quite well.

The flat dome of the bulb *f* must at its upper side be able to retain an air-bubble without letting it ascend to the bulb *e* through the communicating tube. If fresh gas is evolved in the liquid in *f*, it diffuses little by little into this air-bubble, which has to stand only the pressure of the very short superincumbent column of water (in my apparatus this is 10 millims. high). The bubble in the bulb *f* consequently becomes gradually bigger, and in fact the mixed gas under these conditions takes up more than 1000 times as great a space as it would do under atmospheric pressure, so that the most excessively minute quantities collected in the course of a day announce their presence. I measured the diameter of the bubble with a millimetre-scale laid above it, in order to ascertain whether it had remained of the same size or had increased.

If the bubble becomes too great, then one can let a portion of it ascend to *e* by tilting the apparatus. It may be remarked here that the short oblique arm of the tube at *e* is not, as it appears in the drawing, bent to the left but to the front (which could not be conveniently drawn), so that when, after closing the tap *b*, one tilts the upper end of the apparatus towards the front, the air-bubble can ascend.

Every day a sufficient quantity of quicksilver is poured through the apparatus, so that the gas that has diffused into the upper space *d* is always removed again, and the apparatus remains constantly in the same evacuated condition.

For generating the current I used three iron-ferric-chloride-carbon cells*.

The resistance in their circuit amounted to 3000 mercury units, relatively to which their own resistance of about 75 units* was so small that any small variations in their resistance did not come into consideration. The cells remained thus without interruption in closed circuit, in order to maintain them in the most constant condition possible, and in this case their electromotive force falls off very slowly. Every day the strength of the current excited by these cells through this resistance was compared with that of a tightly shut-up calomel cell which otherwise remained untouched and with the circuit open, and then the amount of resistance was calculated which one must interpose between the wires leading to the cell in order to obtain the desired electromotive force in the latter. This force I diminished by small degrees from day to day, in order to find the limit. The convection-current going through the cell was in these cases so weak that it produced no diminution in the electromotive force that need come into consideration.

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* [These cells are of the type devised by Dr. Conrad Pabst, of Stettin. The use of ferric chloride in cells is not new; it was suggested by Liebig, used also by Buff, in England by Reynolds, and in France by Basset. In Pabst's cell the anode is a small block of wrought iron, the kathode, presenting at least three times as much surface as the anode, is a plate of carbon impregnated with iron rust by repeated dipping into a strong solution of iron and subsequent heating in an open fire. Both anode and kathode are supported on a slip of ebonite placed across the cell. The exciting liquid is an 11-per-cent. solution of ferric chloride. These cells do not easily polarize on short circuit. One of them examined by the writer gave a current of $\frac{1}{3}$ ampere for three weeks without intermission. When first set into action there is a slight evolution of chlorine, and a partial reduction of the ferric chloride to ferrous chloride; the latter absorbs oxygen from the air, depositing hydrated ferric chloride at the bottom of the cell. The action, when once the evolution of chlorine has begun, is wonderfully steady. The E.M.F. is about 0·78 volt. The cells require to be protected from the light either by using jars of dark glass or stone-ware, or by keeping in the dark, and the solution must not be allowed to become too concentrated, otherwise the cell gets choked with oxychloride of iron.—S. P. T.]

The calomel cell was from time to time compensated many times with a current of which the electrolytic silver-equivalent was determined, and its electromotive force reduced to volts. Its value was 1·034 volt.

The limit for the evolution of gas I found to be between 1·64 and 1·63 volt for a pressure of mixed gas equal to that of 10 millims. of water. If one could work in a room of constant temperature, the determination could be made still more exactly. Since the value of the electromotive forces of the various battery elements did not change in equal proportions with temperature, and since also a rise of temperature must set free out of the liquid a little of the dissolved gas, small variations in these values might occur.

In order to establish the main point that the electromotive force necessary for decomposition is dependent on the pressure of the mixed gases, there was joined up in parallel with the previously described barometric cell a similar one of earlier construction, which had a slightly modified form of vessel and was without a tap. This was to begin with pumped empty; the mixed gases were evolved in it up to atmospheric pressure, so that the quicksilver stood almost equally high in the two limbs of the barometer, though naturally somewhat changing with changes in the pressure of the air and in the temperature. This could be joined in the circuit as a shunt at the same time as the exhausted cell, but so that its points of attachment to the wire of 3000 mercury-units [resistance] took in between them a somewhat greater resistance of the battery-circuit than those of the other cell. There was no reason on this account to fear a mutual disturbance of the two branch conductors, certainly not within the limits of accuracy hitherto attained, since both cells when in the polarized state have, as we shall forthwith describe below, conducted into them only very inconsiderable fractions of the battery-currents, and consequently do not alter in any noticeable degree the values of the potential of the various parts of the circuit. The position of both the quicksilver summits was read off every day with the kathetometer, and the pressure of the gas in the upper space in the cell calculated, with correction for the pressure of aqueous vapour. It was found that this pressure showed no further increase at 1·79 volts, but did at 1·82 volts. In order to attain more exact determinations between these limits, the method must be somewhat altered so that the temperature can be better controlled.

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* [I do not understand this; for the three Pabst cells used by Professor von Helmholtz are identical in construction and size with those which the writer has, of which the average internal resistance is about 2 ohms. Three such in series might have a resistance of 7·5, but not of 75 ohms.—S. P. T.]

Since the first question with which we are concerned is to determine the inferior limit of pressure* at which no decomposition takes place, it is safer not to take the above-named limit of 1·79, which corresponds to the initial condition of the value immediately after the daily adjustment, but the final condition, as it resulted next day after a fresh comparison with the calomel cell. In that case we must go down to 1·78, or even to 1·775.

Further, it must be taken into consideration that one part of the electromotive force corresponds to the differences of potential which the current produces in the resistances. In the air-free cell the current was so small after polarization was set up, that it only amounted to about a hundredth part of the convection-current flowing through the non-exhausted cell. This latter stronger current amounted to about $\frac{1}{57021}$ of an *ampere*, and encountered in the battery about 75 ohms, in the cell (the resistance of which was calculated approximately from the dimensions and distance apart of its wires and from the conducting power of the sulphuric acid) about 25 ohms, besides a varying part of the great resistance-scale, which did not amount to more than 100 ohms. This gives, in the most favourable case, a consumption of 0·0035 volt, which must be deducted from the electromotive force as being required to overcome the resistance.

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* [Query: "electromotive force"?]

Finally, it is to be remarked that the cell filled with gas at 742 millims. certainly did not nearly so easily indicate an increment or decrement of the gas as the exhausted one, in which the volumes of gas are nearly 1000 times greater. On the other hand an excess of 0·01 volt in the small resistance of at most 200 ohms in the circuit of this cell must yield 6·7 cubic centims. of gas in 24 hours, which could not have been overlooked in the barometer-tube of 5 millims. internal diameter; so that there can not have been made in this direction any error that could come into consideration.

For the influence of pressure upon the electromotive force I have developed the following expression (Proceedings of the Berlin Academy, 31 May 1883, p. 660, equation 3 *c**) :—

$$A = A_o + 10^{-7} . \eta . \theta \left\{ R_h \frac{2\alpha_h}{2\alpha_h + \alpha_o} \log \left(\frac{p_h}{p_a} \right) + R_o . \frac{\alpha_o}{2\alpha_h + \alpha_o} \log \left(\frac{p_o}{p_a} \right) \right\} .$$

Here p_a is the atmospheric pressure, p_h and p_o are the pressures of the hydrogen and of the oxygen standing above the liquid; α_h α_o are the atomic weights of the same elements; θ the absolute temperature in centigrade degrees.

$$R_h = \frac{p_h . v_h}{\theta} = 41461000 . \frac{\text{centim.}^2 g}{\text{sec.}^2},$$

where v_h is the volume of 1 gramme of hydrogen; R_o is the corresponding constant for oxygen; and η the quantity of water decomposed in a second by 1 *ampere*. According to the latest determinations of F. Kohlrausch,

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* [*Vid. supr.* p. 91.]

$$\eta = 0{\cdot}00009319.$$

When pure mixed gas stands over the liquid, as in our researches, and we denote by p its pressure, so that

$$p = p_h + p_o,$$

then the part of the electromotive force which changes with the pressure will be

$$\mathrm{A}_1 - \mathrm{A}_2 = \frac{1}{6} . 10^{-7} . \eta . \theta . \mathrm{R}_h . \log\left(\frac{p_1}{p_2}\right) = 0{\cdot}018868 . \log_\epsilon\left(\frac{p_1}{p_2}\right).$$

The pressure in the exhausted tube amounted in the mean to 10 millims. of water, and in the other tube amounted, as corrected for the pressure of aqueous vapour, to 742 millims. of mercury. For this proportion of the pressures our formula gives a difference of electromotive force of 0·1305 volt. We had 1·64 volt for the last residue of gas evolution, and should conclude therefrom that in the other cell the evolution of gas would have its limit at 1·77. This corresponds also with the result of experiment as given above, when the corrections are taken into account, within the limits of accuracy hitherto attainable.

The determination of the limit for the higher pressure of mixed gas I hope to be able to define still more closely and also to make observations free from asymmetry of the electrodes, which is not without influence, and which cannot be entirely avoided when using blown glass cells.

If we wanted to proceed to higher pressures we should be obliged to increase the pressure of one atmosphere in the same proportion, namely to more than 1000 atmospheres, in order to attain a rise of the electromotive force through the same difference of 0·16 volt; that is to say, in order to increase it from 1·79 to 1·95 volt. But this will not succeed, for already Dr. Werner Siemens has found that at a certain elevation of pressure the mixed gas is spontaneously kindled*.

* See Werner Siemens's collected *Abhandlungen und Vorträge*, p. 445, *note*, where a current from 3 to 4 Daniell cells ceased to give decomposition when the pressure became very great. With 10 Daniell cells the mixed gas repeatedly ignited itself.

There is still this fact to be considered, that the greater the pressure the more strongly does the liquid become charged with dissolved gases. And the more strongly do the convection-currents flow, which discharge an ever-increasing fraction of the current without electrolytic decomposition. Thereby, in the measurements, the effect of the resistances in the cells becomes continually of greater importance, and the evolution of heat in them continually more disturbing. I have therefore preferred to confine myself to the very weak currents here used, and to work with low pressures.

[The following papers on subjects allied to Electrolysis have also been published by Professor von Helmholtz, and most of them have already been translated into English :—

Ueber galvanische Polarisation in gasfreien Flussigkeiten. *Monatsberichte d. Berl. Akad.* 1873, p. 584 ; Pogg. *Ann.* Bd. cl. p. 483 ; *Phil. Mag.* [4] xlvii. p. 145.

Bericht über Versuche des Hrn. Dr. E. Root aus Boston, die Durchdringung des Platins mit electrolytischen Gasen betreffend. *Monatsb. d. Berl. Akad.* 1876, Mar. 16; Pogg. *Ann.* Bd. clix. p. 416 ; *Phil. Mag.* [5] ii. p. 153.

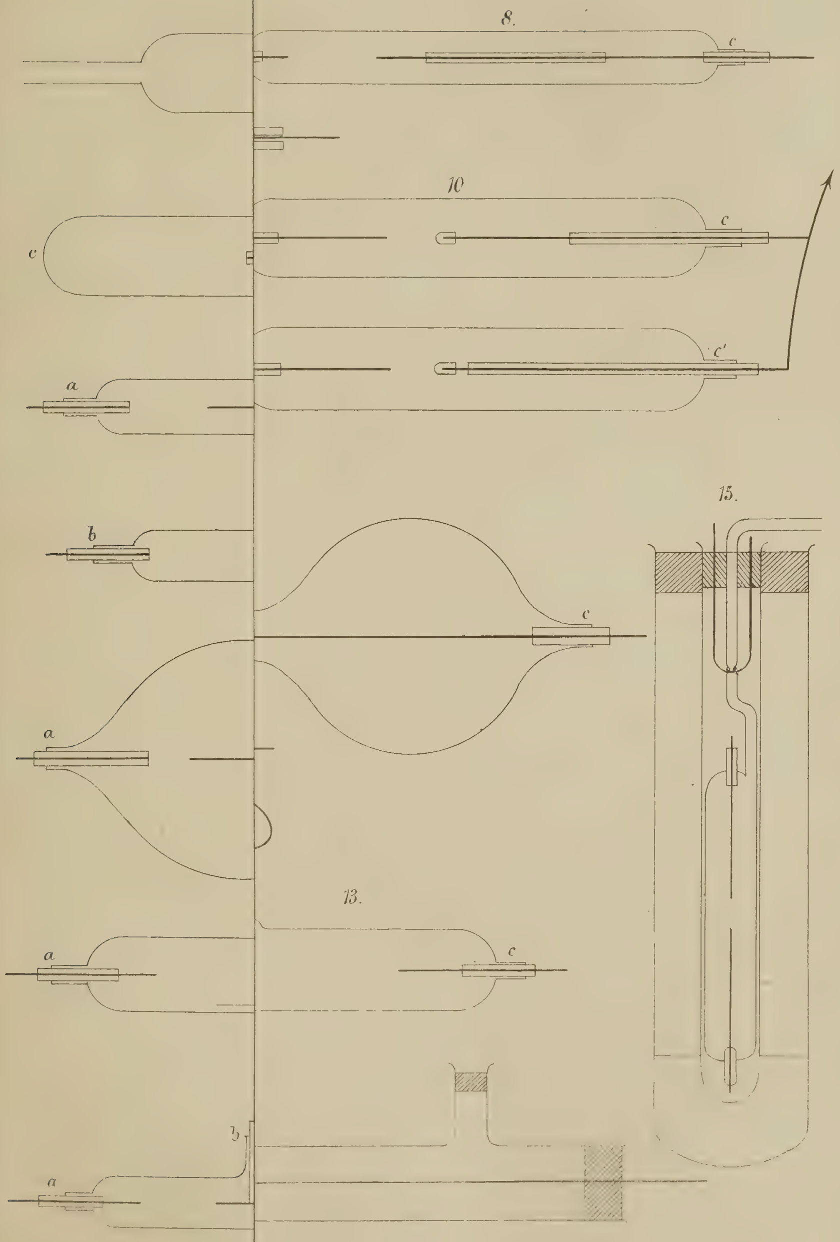
Ueber galvanische Ströme, verursacht durch Concentrations unterschiede ; Folgerungen aus der mechanischen Wärmetheorie. *Monatsb. d. Berl. Akad.* 1877, Nov. 26 ; Wied. *Ann.* Bd. iii. p. 201 ; *Phil. Mag.* [5] v. p. 348.

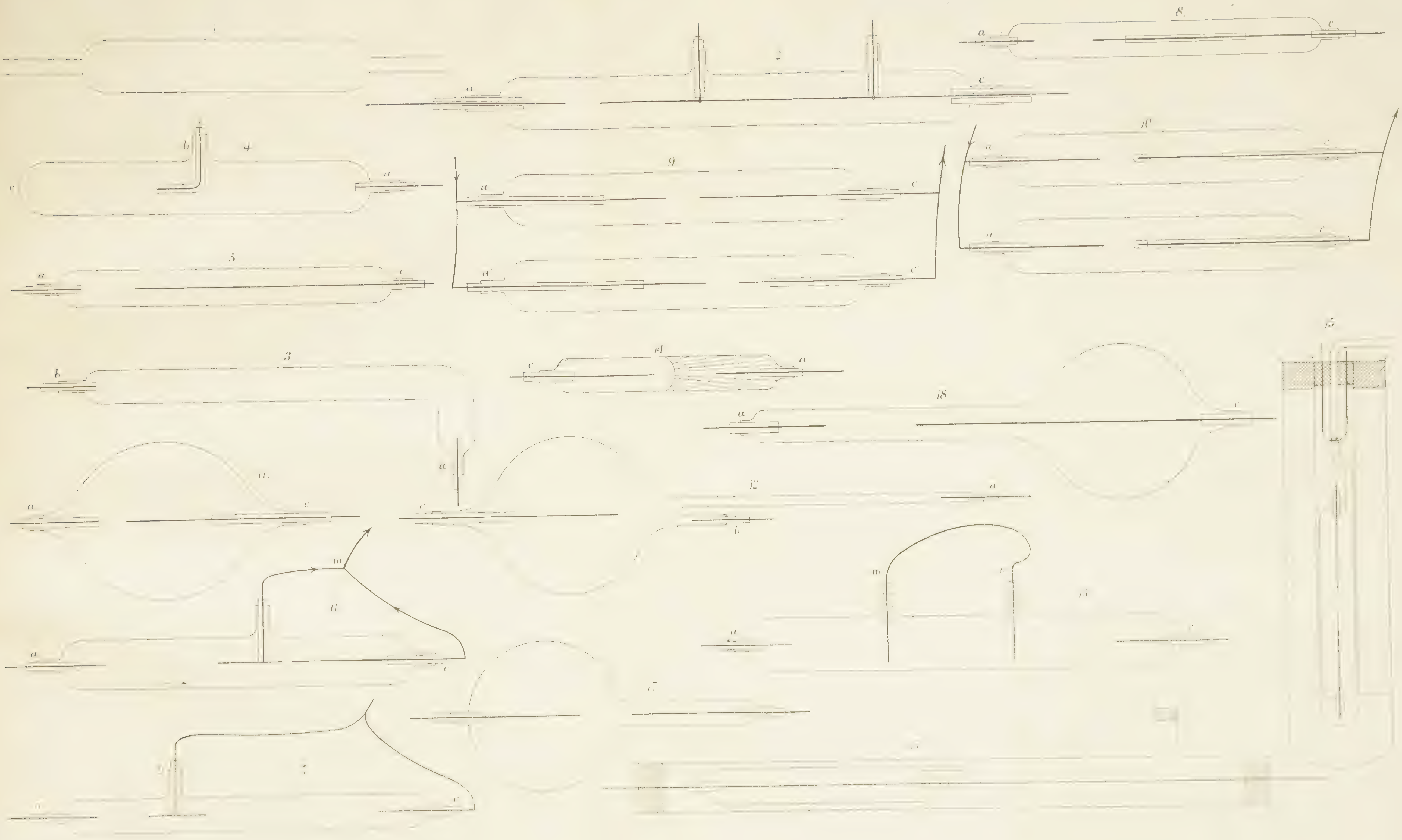
Ueber Bewegungsströme am polarisirten Platina. *Monats. d. Berl. Akad.* 1880, Mar. 11 ; Wied. *Ann.* Bd. xi. p. 737.

Ueber galvanische Polarisation des Quecksilbers und darauf bezügliche neue Versuche des Hrn. Arthur König. *Monatsb. d. Berl. Akad.* 1881, Nov. 3.

On the Modern Development of Faraday's Conception of Electricity. *Journ. Chem. Soc.* (Faraday Lecture), 1881, p. 277.]

Hittorf. Physical Mems. Pl. I.

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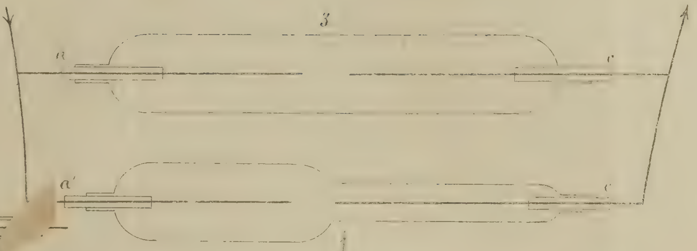

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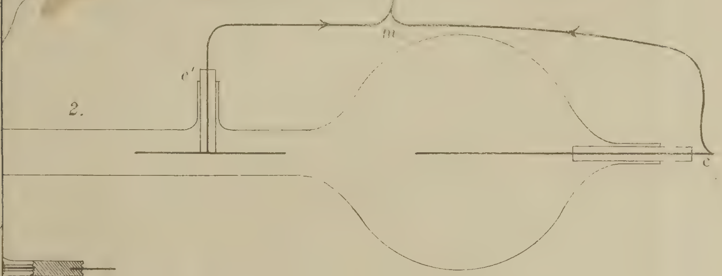

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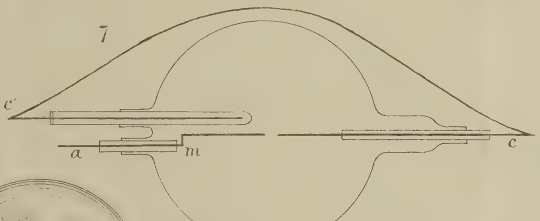

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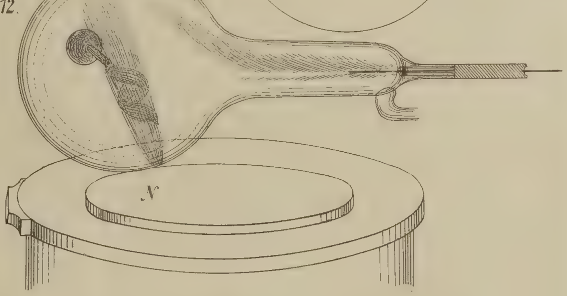

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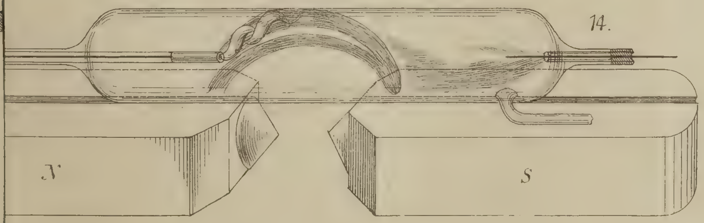

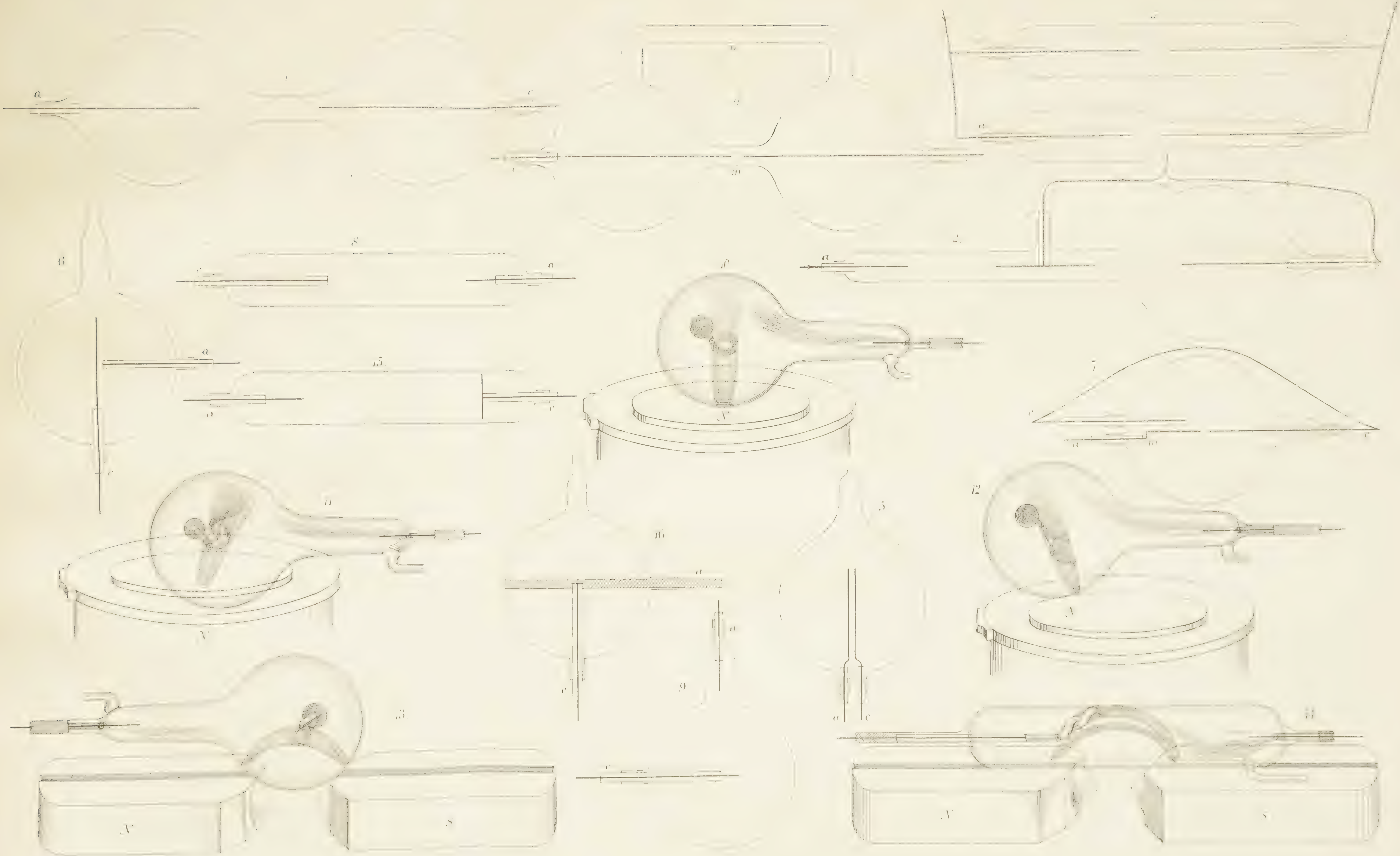
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PHYSICAL MEMOIRS.

ON THE CONDUCTION
OF
ELECTRICITY IN GASES.

BY

PROFESSOR W. HITTORF.

PART I.

Ueber die Elektricitätsleitung der Gase. Poggendorff's *Annalen*, vol. cxxxvi. pp. 1-31, 197-234, 1869.

[PLATES I. & II.]

THE most obscure part of the present science of Electricity is undoubtedly the process by which the transmission of the current is effected in gaseous bodies. While for solid and liquid conductors, whether they are metallic or electrolytic, the relations between the facts have been collated, and have acquired a common bond in Ohm's law, our knowledge of the conductivity of gases, notwithstanding the endeavours of distinguished physicists, is of a decidedly fragmentary kind, and rests mostly on observations which are imperfect and isolated. The theory of the electrical spark, the longest known and the most striking of all electrical phenomena, can only be established when the condition of our knowledge is improved.

In the last twenty years two arrangements have materially promoted the study of the spark, namely, Ruhmkorff's induction apparatus provided with Fizeau's condenser, and the mercury-pump of Dr. Geissler.

Gases at low temperatures have an almost infinitely great resistance for electricity of such low tension as is furnished by a voltaic element, and only begin to lose this insulation at a red heat. If they are to transmit a discharge at ordinary temperatures, the electricity must have far higher tension. The only source hitherto available, the frictional machine, is but little productive, and the induction-coil furnished therefore a welcome supplement. The one used in the experiments of this research is an ordinary Ruhmkorff's coil, 30 cm. in length by 16 cm. in thickness. The other instrument mentioned above was of not less use. For the electrical phenomena which are characteristic of the gaseous state of aggregation, are most favourably accessible to observation when the medium has become very rarefied. Ordinary air-pumps do not enable us to push the rarefaction lower than a pressure of from 3 to 2 mm. of mercury. The special features of gaseous conductivity are most striking below this degree of rarefaction, and in many cases are only then to be observed. Hence Dr. Geissler did a great service to this branch of Physics when, by means of the barometer, he showed how gases could be conveniently and rapidly brought to any desired rarefaction.

2. I may perhaps assume that the arrangement of Geissler's aspirator is sufficiently known, and I need only mention a small modification which I have made in it. In order to remove the moisture from the inside of the glass tube, the inventor interposed a vessel containing a drying substance, for which purpose he used concentrated sulphuric acid. This liquid has so small an absorption for air and ordinary gases, that in most cases it does not come into consideration. In the present case, however, it prevents the extreme rarefaction of which the pump is capable. For when the air has been removed from the tubes as completely as possible, the sulphuric acid is seen to liberate minute bubbles, often for hours together. On replacing sulphuric by anhydrous phosphoric acid, I was able to produce a condition such as exists in the Torricellian vacuum of the best barometers. When the air is completely removed from the pump, the ascending mercury in striking against the stopcock produces the peculiar sound which is characteristic of a carefully boiled-out barometer. As long as the shock is somewhat dull, a trace of air can still be withdrawn when the mercury is run off, and one must not be annoyed at having to continue the operation.

The manometer which is affixed to my pump has only short limbs, but is 30 millim. wide. The meniscus of the mercury is illuminated by a lamp with an opal glass globe, and the difference in height measured by a Meyerstein's cathetometer. Some time, however, before the mercury of the pump strikes sharply, such a difference can no longer be observed, for if the difference is less than $\frac{1}{20}$ mm. it cannot be distinctly perceived in this way.

3. The absolute vacuum can of course be as little obtained in the interior of a Geissler's pump as in a boiled-out barometer. It is easy to demonstrate the presence of mercury in the system of tubes by enclosing a weighed strip of silver and then exhausting. In an experiment which I made in this direction the strip, which had a surface of nearly 18 sq. cm., weighed originally 3·629 grammes, and after it had been exposed for eight days at a temperature of 16° to 17°·5 C. it weighed 3·6335 grammes. It had therefore taken up 0 0045 gramme of mercury, and when heated it gave off a distinct cloud of vapour.

4. The aspirator presents a number of advantages for the investigation of the electrical spark which cannot be too highly appreciated. While the gas passes through all degrees of rarefaction, it remains accessible to the discharge, and thus enables us to observe the changes which the luminous phenomena of the current undergo. The liquid mercury, moreover, does not remain in contact with the experimental tube, and a residue of individual drops is not to be feared. The rarefaction can lastly be carried further than in the best Torricellian vacuum, provided the tube be simultaneously heated to as high a temperature as the glass will bear, and the medium be fixed by sealing the tube while in this expanded condition. The deportment of such tubes towards the electrical current will be subsequently discussed.

5. It was frequently necessary in my experiments to change the shape and dimensions of the metallic conductors which served as electrodes, and hence if they had been fused into the glass, as in Geissler's tubes, I should have needed a great number of tubes. If the tubes are not to be heated, closing with sealing-wax is sufficiently efficient, and has the advantage that it is easily done and undone. The ends of the tube which I used are usually narrowed off, as shown in fig. 1, Plate I., and capillary tubes are fused in them through which the conducting wires pass. For greater certainty of closure the melted sealing-wax must be drawn for some

distance into the capillary tube. If the cement is only at those parts which the electrical current does not reach, these tubes can be as easily exhausted at ordinary temperatures as can those in which the wires are fused into the glass. If, however, the electric light passes over the sealing-wax, the high temperature gives rise to gaseous products of decomposition which may have a disturbing influence. In consequence of changes of temperature the sealing-wax readily cracks, and accordingly does not enclose the gas so perfectly for a long time as do Geissler's tubes. In most cases I used aluminum for the electrodes, since this metal, as Geissler found, does not volatilize when used as the kathode, and hence does not produce a deposit on the surrounding sides.

§ 2.

6. Faraday, so far as my knowledge of the literature extends, was the first to call attention to the peculiar appearance of the electrical discharge in rarefied air. In the thirteenth series of his Experimental Researches on Electricity, which appeared in the year 1838, he says :—

"§ 1544. I will now notice a very remarkable circumstance in the luminous discharge accompanied by a negative glow, which may perhaps be correctly traced hereafter into discharges of much higher intensity. Two brass rods 0·3 of an inch in diameter entering a glass globe on opposite sides had their ends brought in contact, and the air about them very much rarefied. A discharge of electricity from the machine was then made through them, and whilst that was continued the ends were separated from each other. At the moment of separation a continuous glow came over the end of the negative rod, the positive termination remaining quite dark. As the distance was increased a purple stream or haze appeared on the end of the positive rod, and proceeded directly outwards towards the negative rod, elongating as the interval was enlarged, but never joining the negative glow, there being always a dark space between. This space of about $\frac{1}{16}$ or $\frac{1}{20}$ of an inch was apparently invariable in its extent and its positive relation to the negative rod, nor did the negative glow vary. Whether the negative end were inductric or inducteous the same effect was produced. It was strange to see the positive purple haze diminish or lengthen as the ends were separated, and yet this dark space and the negative glow remained unaltered."

For a long time these phenomena attracted no further attention. They only excited general interest when in the fifties they were obtained in so striking a manner in the discharge of Ruhmkorff's coil through rarefied tubes.

7. No medium is more suited for their observation than air, or more correctly nitrogen, to the particles of which the light of the spark in the tube is mainly due. The negative and positive lights here have different colours, the former is blue, the latter reddish yellow, while the other gases usually glow with the same colour for the whole path of the current.

The negative light of air is further distinguished from the positive by another peculiarity. When its temperature is very high it excites a bright fluorescence on the surface of the glass which it touches, while the positive light of this medium does not produce this. Ordinary glass is known to fluoresce with a yellowish green; lead glass with a blue colour.

In the following description of the phenomena which the electric discharge produces, we shall assume that the medium is air, although they belong to all gases.

8. The three parts—the positive light, the dark space, and the negative glow-light—occur at all densities of the enclosed medium, if the electric discharge be of a measurable duration. At the ordinary pressure the blue glow-light on the surface of the electrode only covers a little spot in the sheath of light which follows the momentary discharge; the size of this spot is very little different from the section of the sheath, and, with Neef and Du Moncel, we must make use of a magnification in order to distinguish the dark space in the lights of different colours. The further the rarefaction is carried, the greater is the surface of the electrode over which the same discharge emits blue light. It increases with particular rapidity when the tension is reduced below 2 mm. When a wire 82 cm. in length was fastened as kathode in the axis of a tube 60 mm. in width, the glow, which always begins on the end nearest the anode, extended over the entire length at a pressure of 0·33 mm. The surface of a wire of any given

length will be seen to be surrounded by it if the rarefaction is sufficiently great and the diameter large enough.*

9. As the density decreases the glow-light extends, not merely over the surface of the kathode, but also further into the surrounding space. The thickness of the blue envelope which surrounds the negative pole increases again with particular rapidity when the pressure has sunk below 2 mm., and at the most extreme rarefaction fills the widest tubes.

For the same density of the medium, the glow-light extends so much the further from the kathode the smaller is its surface. At the same time the tension which the same discharge produces on the electrodes increases, and the fluorescence of the glass becomes more brilliant. In order to observe this, two equal cylindrical tubes, which had electrodes of different lengths in the axes, were attached to the pump and interposed in series in the same induction-current, and such rarefaction produced that both kathodes were entirely surrounded by the glow-light. This experiment is particularly instructive when the free surface of one electrode is made as small as possible by sliding it in its capillary tube, and thus approximately a point-like kathode is produced. A beautiful blue hemisphere of glow-light is now formed about it, the radius of which is over 1 cm. at a pressure at which the envelope of a longer kathode has a scarcely perceptible thickness, and which radius very rapidly increases as the pressure diminishes. So long as it is small the negative light is separated from the positive by a dark space. This disappears, however, and the two lights come in contact when the former has greatly spread out.

10. Any solid or liquid, whether insulator or conductor, which is in front of the kathode shuts off the glow-light which lies between it and the kathode ; there is no deflection from a straight line.

If we take a tube bent at right angles (fig. 3, Plate I.) the legs of which are of very different lengths, and if two point-like electrodes are fastened at the ends, at a sufficient rarefaction the negative light floods the whole of the long limb if *b* is the kathode. If *a* is the negative pole it remains confined to the short leg, and cannot follow the curvature of the tube. The rectilinear propagation of the glow is most distinctly seen when it proceeds from a point-like kathode, and with greater length it causes the surface of the glass to fluoresce. If in such circumstances any object is interposed in the space filled with glow-light, it throws a sharp shadow on the fluorescent side, since its surface just cuts off the luminous cone proceeding from the kathode as apex.

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* The necessity for this condition will be seen from the fourth paragraph.

In the sequel we shall speak of the rectilinear path, or the rays of the glow-light, and shall take each point of the kathode as the apex of a cone of rays.

In any long cylindrical tube which contains the point-like kathode in the axis, the rays strike the sides the sooner the more they diverge from the axial direction. Hence at a greater distance from the kathode, and with a sufficient degree of rarefaction, a pencil of approximately parallel rays of the glow-light remains which will afterwards be of use to us.

11. If the glow-light spreads out in right lines from the points of the kathode, it must be independent of the direction of the positive rays; this is very distinctly seen when the point-shaped kathode is turned away from the anode.

A capillary tube *b*, which encloses a wire so as only to leave the terminal section bare, was bent at a right angle, as shown in fig. 4, Plate I., and fused in the middle ot a wide tube. A second point-shaped electrode *a* was fused at the end turned away from the section *b*. If *b* is the kathode, the glow-rays flood the space *bc* more and more as the density decreases; they therefore diverge increasingly from the anode and from the positive light on the path *ab*. The distinction between the transmission of the negative and that of the positive light is very distinctly seen when the functions of the two electrodes are interchanged, that is when *b* becomes the anode, and *a* the kathode. The red positive light now curves directly behind the section *b*, and pursues the direction towards *a*. The negative light of *a*, on the contrary, flows forth in a right line, and at a greater rarefaction passes to any extent over *a* quite independently of the fact that it here crosses the anode. The latter also takes place when the surface of the wire *b* is quite bare. Even when the anode, consisting of a long wire, is in the axis of the tube and opposite the negative section (fig. 5, Plate I.), the brush floods the space *ca* notwithstanding the presence of the positive pole.

12. The glow-light on the path on which it flows from the kathode does not appear homogeneous but consists, as is well known, of three layers which are parallel to the negative surface, and can be distinguished by their different luminosity. While the number of layers in the positive light varies greatly with the dimensions and shape of the vessel and the density and nature of the medium, it is constant under all conditions with the negative light. A narrow, often difficultly perceptible bright band directly surrounds the kathode. To this follows a broader, less luminous, and therefore transparent layer, which again stands out from the last, which is brightest and broadest. The breadth of these layers increases continuously as the density of the gas is diminished. In like manner for the same density the breadth increases with the intensity of the current.

§ 3.

13. The glow is manifestly the process by which the passage of the current is effected from the particles of the gaseous medium to those of the solid or liquid kathode. If the wire which is intended for the latter be chosen of two or more pieces, and, as shown in fig. 6, Plate I., be connected outside the tube only, we can learn from the intensities of the current in the external connecting wires *bm* and *cm*, what share of the total current each portion of the kathode acquires.

14. For this and the following determinations, such a resistance was interposed in the path *bm*, by means of a rheostat and suitable coils, that the current, which the wire of a sensitive galvanometer shunted from it, produced a suitable deflection of the needle. The resistance necessary for this (r') is so small in comparison with that of the gaseous medium that it exerts no appreciable influence on the division of the entire current. For in order to reduce the deflection by an appreciable amount, in addition to the shunted resistance it was necessary to introduce into one of the branch circuits *bm* or *cm*, a resistance a thousand times as great. If R is the resistance of the galvanometer wire, and

I the strength of the current in it, the strength of the current in the part *b* of the kathode is $I\left(\frac{r'+R}{r'}\right)$.

Proceeding in the same way for the path *cm*, and if r'' again signifies the resistance from which the galvanometer wire diverts that current which gives the same deflection, the strength of the current in *cm* will be $I\left(\frac{r''+R}{r''}\right)$.

Accordingly the ratio of the currents which enter the parts of the kathode *b* and *c* is

$$\frac{\frac{r'+R}{r'}}{\frac{r''+R}{r''}},$$

or nearly $\frac{r''}{r'}$, inasmuch as the resistance of the long and thin galvanometer wire was ordinarily more than a thousand times as much as r' and r''*.

The induced current produced by a single break of the inducing one is not sufficient for the method described. By means of a Foucault's contact-breaker, worked by a separate voltaic element, a series of induction-currents must be produced and passed through the tube. A tangent-galvanometer is inserted in the path of the inducing current. The needle does not indeed acquire a fixed position, for the point of the contact-breaker does not always remain for the same time in contact with the mercury. But it may easily be made to oscillate continuously about the same mean position. The deflection which the needle of the galvanometer experiences from the shunted portion of the galvanometer is thus quite steady, and shows that the mean intensity of the latter remains constant.

In order to attain this steadiness, the mercury of the contact-breaker must not be too much disintegrated by the spark, and, therefore, driven into the alcohol above. Hence after long usage both liquids must be replaced by fresh. I have also found it advisable to substitute for ordinary alcohol the less volatile amyle alcohol. The contact-breaker must not bend downwards in consequence of the oscillatory motion and must be firmly clamped.

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* If a sensitive reflecting galvanometer is available the same resistance can be introduced into both paths, and the two deflections be observed which are produced by the branch circuits. Their ratio is that of the desired strengths of currents.

It lies in the nature of the case that these determinations have not that degree of accuracy which is attainable by using continuous currents. They are, however, sufficiently precise to throw light on a number of important questions.

The induction-current which was produced on closing the voltaic element was always kept from the tube by the interposition of a thin layer of air, and all connexions of the various wires were effected by binding-screws.

15. The measurements of the intensities of the currents thus made show that the wires *b* and *c* (fig. 6, Plate I.), when uniformly coated with the glow-light, take it almost proportionally to their lengths. This proportionality only commences when the pressures of the gaseous medium are below 2 mm., and continues on further rarefaction if the tube surrounding the kathode is of sufficiently large diameter. The section which the current assumes at the kathode is therefore very great in comparison with that existing in the part of the tube which is filled with positive light. As, notwithstanding this small density of the current, the gas about the kathode is strongly heated, resistances must be formed there in comparison with which those that effect the production of the positive light are infinitely small. When the latter occurs, the current, at the small density which exists at the kathode, cannot heat the gas so highly as to produce spontaneous luminosity. This is shown by the dark space between the positive and negative light, and therefore at the place at which the former takes the section of the latter. This also explains how that part of the negative electrode which is further from the anode, can, for the same surface, take approximately the same portion of the current. For the resistance which the circuit, from the near to the more distant piece, offers is small in comparison with that which the transition to the kathode presents.

This conception acquires a beautiful confirmation in a phenomenon which always occurs when the two portions of the kathode are separated from each other by a longer interval in the tube (fig. 7, Plate I.). As soon as the blue glow-light forms on the further wire *c*, the distance *bc* fills with a reddish-yellow positive light, which in narrower tubes is just as regularly stratified as that which lies between the anode *a* and the nearest part of the kathode ; only it is not quite so luminous. It is smaller at the glow-light about *b* than at that about *c*. Where, therefore, the current has changed from the large section which it has about the kathode *b* into the small one of the cylindrical tube, the gas again becomes self-luminous, which of course appears so much the feebler than that of the path *ab*, the greater is that part of the current which *b* has already taken. The same phenomenon may also be produced in any cylindrical tube with a long wire-like kathode, if the middle part of the latter is covered with an insulator—a glass tube fused on it (fig. 8, Plate I.). The reddish-yellow stratified light occurs here if the uncovered surface is coated with blue glow-light.

16. If two tubes are inserted in parallel in the induction-current (fig. 9, Plate I.), the discharge cannot be simultaneously produced in each, at a great density of the gaseous medium, however equal we seek to make the electrodes, their distance, the width of the tubes, and the pressure of the same gas. The current always passes through one tube only, and when the tubes have been made as equal as possible, it passes first through one and then through the other.

If, however, the rarefaction has become so great in both tubes that the negative wire would become covered with glow-light for a length equal to both together, then from that time the tubes are filled uniformly with light. The division of the current ensues at these small densities even when there are great differences in the arrangement of the apparatus. Hence by measuring the intensities of the current in both branches, the influence of these differences on the circuit may be ascertained.

17. I begin with the variation caused by changes in the length of the negative wire. In order to give the reader an idea of these measurements, I will here give the numbers in detail.

Both glass tubes were of the same piece, of 46 mm. diameter. A greater width would have been still more convenient. Two pieces of the same platinum wire, of 0·66 mm. diameter, were taken, one of which projected 26·5 mm. and the other 103 mm. from its capillary tube, and whose free surfaces were therefore in the ratio of 1 : 3·89. These were fused at equal distances opposite the equally long and thick anodes. The tubes contained hydrogen, and the determinations were first made at a pressure of 1·35 mm. Two equal Bunsen's elements furnished the current, which, while the Foucault's contact-breaker was at work, made the needle oscillate about 41°. In order to shunt through the galvanometer such a proportion of the induction-current which traversed the wire with the long kathode that the deflection of the needle should be 10°, it was necessary to use 2 × 38 cm. of the platinum wire of my rheostat. In order to obtain the same deflection of 10° with the current in the tube with the short kathode, a length of 2 × 163 cm. was necessary. The intensities in the two tubes were therefore as

$$\frac{163}{38} = 4·29.$$

Instead of the deflection 10° of the galvanometer, one of 20° was chosen. In order to obtain this with the current in the tube with the long kathode, the galvanometer wire required 2 × 92 cm. of the rheostat. For the same effect a resistance of 2 × 384 cm. was necessary in the current of the tube with the short kathode. The ratio of the intensities is

$$\frac{384}{92} = 4·17.$$

A deflection of 30° was finally taken for the needle of the galvanometer. This required a resistance of 2 × 153 cm. in the branch containing the long kathode, and the resistance 2 × 653 in the branch with the short kathode. The ratio of the intensities is $\frac{653}{153} = 4·27$.

The inducing current was produced by three Bunsen's elements, and gave a deflection of 52°·5. To produce a deflection of 20° in the galvanometer,

The current of the long kathode required a resistance of . .	2 × 53 cm.
,, ,, short ,, ,, ,, . .	2 × 224 ,,
Ratio of the intensities	4·23

For a deflection of 30° in the galvanometer,

The current of the long kathode required a resistance of.. 2×88 cm.
„ „ short „ „ „ .. 2×382 „

Ratio of the intensities .... 4·34

The hydrogen gas was reduced to about half the pressure, namely 0·72 mm.

Two Bunsen's elements furnished the inducing currents.

For a deflection of 20° in the galvanometer,

The current of the long kathode required a resistance of.. 2×100 cm.
„ „ short „ „ „ .. 2×422 „

Ratio of the intensities........ 4·22

For a deflection of 30° in the galvanometer,

The current of the long kathode required a resistance of.. 2×166 cm.
„ „ short „ „ „ .. 2×701 „

Ratio of the intensities .... 4·22

Phenomena entirely similar were observed with nitrogen and wire-shaped kathodes of aluminum, the ratio of whose surfaces was 5 : 3. In both tubes, in which there was the same difference of potential at the electrodes, the negative luminous envelopes were equal both in brightness and in thickness; whereas, as has been already observed in art. 9, there were considerable differences in this respect when they were joined in series, or when they were each placed separately in the circuit, and the conduction took place at various differences of potential.

At great rarefactions the current divided almost in the ratio of the surfaces which the negative light covered. The result given by the tube (fig. 6, Plate I.) is therefore produced here again. The resistance offered by the space from the anode to the glow-light must be small in comparison with that of the kathode.

18. The influence of the magnitude of the negative pole-surface on the conduction of the induction-current, which Gaugain first observed, is most apparent with the method pursued. It appears much smaller if the tubes are inserted separately in the path of the current, and the resistance of each is determined by the decrease of the intensity.

Thus a tube of 46 mm. diameter containing hydrogen at 0·6 mm. pressure, and provided with two equally thick aluminum wires of the lengths 85 mm. and 20 mm., at a distance of 29 mm., gave the following results. When one element excited the Ruhmkorff the intensities of the induced current were as 1·367 : 1, according as the long or the short wire served as kathode. In order to obtain the same results after removing the tube, it was necessary to insert lengths of 193 and 347 mm. of a capillary tube, containing solution of zinc sulphate, between amalgamated zinc wires. The same experiment was repeated with stronger induction-currents, and the results are given in the following table:—

Number of Elements.	1	2	3	
Intensity of the induced current ...	1	2·603	4·132	When the kathode was 20 mm. long.
	1·367	3·55	5·68	,, ,, 85 mm. ,,
Resistance............	347	250	225	,, ,, 20 mm. ,,
	198	145	132	,, ,, 85 mm. ,,
Ratio of the resistances..............	1·746	1·724	1·704	

The ratio of the resistances is here only 1·75 to 1·7, while that of the negative-pole surfaces is 4·25.

19. It is not difficult to account, at any rate generally, for the causes of these different results. The resistance of a gas which is conveying an induction-current is not constant like that of a metal or of an electrolyte, but changes at each moment. At the beginning of the discharge at a low temperature it is almost infinite ; in consequence of the disengagement of heat it rapidly diminishes, and is less the higher the temperature which the current produces. The resistance of the zinc-sulphate solution which enfeebles the induction-current to the same extent may be regarded as the mean resistance of the gas for the duration of the discharge, provided no opposing electromotive forces come into play. This mean resistance depends, as the table shows, on the intensity of the current, and is less as the latter increases, the higher, that is to say, the temperature rises.

Remembering this, we can understand how the two methods must furnish such different results. If the tubes are singly in the path of the induction-current, the gas about the kathode in the tube with the lesser kathode will be considerably more heated, as there is a smaller mass to conduct. In consequence of this its negative light is brighter, and extends further in the surrounding space. Their mean resistance must be smaller than that of the tube with the long kathode, when the temperatures are the same.

If the tubes are abreast, the advantage is on the side of the large kathode, though in much smaller degree. As the negative light is here much more extended, the cooling by the colder environment is relatively feebler than with the smaller kathode. The tube with the long kathode shunts a portion of the whole current somewhat more than is required by the ratio of the surfaces; instead of the latter, 3·87, the number 4·25 was obtained in the above experiments.

20. The division of the total current between the two tubes also occurs even if one negative surface is one hundred times as large as the other. Thus I joined two tubes containing rarefied air, which were alike in all respects except that the kathode of the one was an aluminum wire 26 mm. in length and 1·5 mm. in diameter, while that of the other was the section of a piece of the same wire. In the latter tube light appeared on this kathode alone, namely, a faint blue flame, otherwise it remained quite dark, and had no red positive light at the kathode. The contrast in luminosity in the two tubes was therefore very great. To this corresponded the difference in the strengths of the currents, which here considerably exceeded that in the areas of the negative surfaces, and increased with increase of the rarefaction.

That the cooling acts by the cold environment was very distinctly seen when a slight modification was made in the experiment. We shall find it is not permissible to consider the surface of the plane cross section as identical, in reference to the disengagement of negative light, with an equally large one of the cylinder. Hence, in order to obtain two cylindrical surfaces of very different lengths as kathodes, I covered the ends of the aluminum wires with glass cups, as shown in fig. 10, Plate I. A length of 2·5 mm. of the one was bare, and of 101 mm. of the other. The ratio of the surfaces was therefore 40·4. Although it was smaller than in the preceding case, no negative light was formed on the small surface, and no current passed through the tube, manifestly because the adjacent masses of glass had too great a cooling influence. It is a matter of course that this tube, under the action of the current alone, obtained an intensely luminous ring of negative light, just as that, which has the section as a kathode, becomes filled under these circumstances with a bright light. The mean resistances are indeed considerably smaller than that of the tube with an extended negative pole, but their ratio is much less than that of the surfaces.

21. Besides the cooling there is another circumstance which makes the intensity of the branch circuit in the tube with the small kathode less than that required by the ratio of the lengths of the negative wires. The resistance of the positive current at the great rarefaction is indeed small compared with that at the kathode, but is not infinitely small. It is necessarily greater in the tube with the short kathode than in that with the long one, for the smaller intensity of the current produces there a lower temperature.

If the resistances in the tube with the long kathode are r'_p and r'_n, and those in the other r''_p and r''_n, the ratio of the intensities of the branch currents is $\frac{i'}{i''}=\frac{r''_p+r''_n}{r'_p+r'_n}$. If this is to coincide with $\frac{r''_n}{r'_n}$, which, apart from the cooling, would be the inverse of the lengths of the negative wires, we must have $\frac{r''_p}{r'_p}=\frac{r''_n}{r'_n}$. For the most part, however, we shall have

$$\frac{r''_p}{r'_p}>\frac{r''_n}{r'_n},$$

as the disengagement of heat is proportioned to the square of the strength of the current, and, therefore, also

$$\frac{i'}{i''} \text{ will be } >\frac{r''_n}{r'_n}.$$

In this discussion of the intensities of the branch currents we need only consider the resistances. If antagonistic electromotive forces occur, they are the same in the two tubes, and are without influence on the partition.

22. The enigmatical resistance at the kathode depends upon circumstances which do not directly originate at its surface; but, as the thermal action shows, extend over the entire neighbourhood. These resistances can only be proportional to the magnitude of the negative surfaces, when the spaces filled by the glow-light are in the same ratio. The equally thick and unequally long wires satisfy these conditions provided we disregard their terminal surfaces. If the negative surfaces differ in shape and curvature, their resistances for the same size must be different.

I selected as kathodes two equally long aluminum cylinders, 1·625 mm. and 10·375 mm. in diameter respectively, and whose terminals and connecting wires were covered with glass. Their free surfaces were therefore in the ratio of 1 to 6·385. They were in glass vessels of equal width (10 cm.), containing hydrogen, at equal and small distances opposite the equal positive wires. The resistances of these two reservoirs, which were placed abreast in the inductive current at pressures less than 1 mm., were to each other in a ratio which was pretty constant about 3, although the voltaic elements used varied between 1 and 3, and the pressures were diminished to 0·01 mm.

When, however, the same cylinders received a galvanoplastic coating of copper, and the glow-light deposited this metal on the glass sides, the ratio varied considerably with the density of the hydrogen.

The phenomena are still more complicated when the negative surfaces also differ in shape. The determinations have no interest from our present point of view, as the means of interpreting them are entirely wanting.

23. The conclusion we drew, that the resistance of the positive light at great rarefactions is small compared with that presented by the neighbourhood of the kathode, may be easily and directly shown to be correct. For if equal electrodes are placed at very unequal distances in two tubes of equal width, the positive light in them being thus of very different lengths, the ratio in which the induction-current divides between them, approaches unity as the rarefaction increases.

In two tubes of 46 mm. diameter filled with hydrogen, two platinum wires 26 mm. in length were fixed at distances of 12 mm. and 146 mm. from the equal anodes. The induction-current which two elements excited passed through the smaller distance only between the electrodes so long as the pressure of the hydrogen was more than 4 mm. From this to a pressure of 2 mm. it mostly divided between the two tubes, though the discharge at the greater distance occasionally failed. The determinations of the current-strengths were made, therefore, below this limit. The short column gives the ratios in which the induction-current divided between the tube with the short and that with the long distance between the electrodes at the pressures specified :—

Pressure of Hydrogen. mm.	Ratio of the Strengths.
1·85	1·65
1·00	1·215
0·55	1·034
0·25	1·049
0·10	1·039

The ratio is therefore constant from the pressure 0·55 mm., as the small differences are within the errors of observation. The small divergence from unity does not depend on the resistance of the positive light, but on inequality of the kathodes. For when the distances were equal the ratio of the intensities of the branch circuits was again 1·034 at a pressure of 0·55 mm.

24. If the distance of the anode from the kathode is small, then at pressures less than 1 mm. a gaseous medium will enfeeble the current mainly by the behaviour of the kathodes ; the resistance of the positive light may be disregarded in comparison with that which occurs in their neighbourhood, and which we will call the resistance of the glow-light. If the negative light has completely covered the surface of a given kathode, and if the rarefaction is continued, the resistance which the latter offers to the current increases more rapidly than the rarefaction.

Two equal ellipsoidal vessels were used for these determinations, of the same shape, and also almost of the same volume as the mercury-receiver of my aspirator (fig. 11, Plate I.) ; they were placed abreast in the current. The length of their great axis was 20 cm., and of the small axis 10 cm. Aluminum wires were used as electrodes; the negative projected 72 mm. and the positive 20 mm. from their capillary tubes, and their ends were 20 mm. apart.

Aluminum was used as the negative metal, for it alone is not volatilized by the glow-light, and does not alter the surrounding mass of gas. Otherwise it is far inferior to platinum for our purposes. Two pieces of the same aluminum wire of equal length, which act as kathodes under the same circumstances, show not only greater differences in resistance than occur with platinum, but these differences vary with the intensity and duration of the current. The surface of the aluminum is loosened by the glow-light, and is thus made non-uniform. Wires of this metal which have served for some time as kathode in a rarefied medium, become covered for longer or shorter distances on the surface with white hairs of alumina, if air is admitted, even after the current has been stopped for some time. The finely divided metal, as is well known, possesses this oxidizability at low temperatures. It is never seen when the aluminum has been the anode.

The two ellipsoidal holders I and II were exhausted with the mercury-pump, and filled with hydrogen of 1·08 mm. pressure. The resistances which they offer to the induction-currents in branching, and which are proportional to the lengths of the rheostat that must be inserted to produce the same deflection of the needle, I will for the sake of brevity, designate by the figures I and II.

When the Ruhmkorff was excited by one element,

$$\frac{\mathrm{I}}{\mathrm{II}} = 1{\cdot}17.$$

When three elements were used, $\frac{\mathrm{I}}{\mathrm{II}} = 1{\cdot}07$.

The pressure of hydrogen in the vessel I was unchanged while the stopcock was turned off and that of II reduced to one half by letting off the mercury.

In this case, with one element $\frac{\mathrm{II}}{\mathrm{I}} = 2{\cdot}34$.

„ with three elements $\frac{\mathrm{II}}{\mathrm{I}} = 2{\cdot}46$.

If it can be assumed that the difference of the kathodes, which existed for the same density of the gas, almost holds at various tensions, the ratio of the resistances at the kathode for equivalent surfaces would have been:—

$$\text{With one element } \frac{\text{II}}{\text{I}} = 2{\cdot}34 \times 1{\cdot}17 = 2{\cdot}74;$$

and

$$\text{with three elements } \frac{\text{II}}{\text{I}} = 2{\cdot}46 \times 1{\cdot}07 = 2{\cdot}63.$$

The hydrogen which the pump had withdrawn from the vessel II, was again restored to it by raising the mercury, and the same pressure was produced in both vessels.

The resistances which the induction-current excited by one element experienced were in the ratio

$$\frac{\text{I}}{\text{II}} = 1{\cdot}204 \text{ with one element,}$$

and

$$\frac{\text{I}}{\text{II}} = 1{\cdot}13 \text{ with two elements.}$$

The contents of II were unchanged, that of I was reduced to one half. This gave

$$\frac{\text{I}}{\text{II}} = 3{\cdot}28 \text{ with one element,}$$

and

$$\frac{\text{I}}{\text{II}} = 2{\cdot}92 \text{ with three elements.}$$

If the same inequality of the kathodes still exists, then, if the latter had been identical, we should have had

$$\frac{\text{I}}{\text{II}} = \frac{3{\cdot}28}{1{\cdot}204} = 2{\cdot}72 \text{ with one element,}$$

and

$$\frac{\text{I}}{\text{II}} = \frac{2{\cdot}92}{1{\cdot}13} = 2{\cdot}58 \text{ with three elements.}$$

The numbers must be regarded as identical with those previously found.

The same determination was made for pressures of hydrogen of 0·5 and 0·25 mm. With the same pressure of 0·5 mm.,

$$\frac{\text{I}}{\text{II}} = 1{\cdot}16 \text{ with one element,}$$

and

$$\frac{\text{I}}{\text{II}} = 1{\cdot}115 \text{ with three elements.}$$

When the capacity of the receiver I was brought to one half, while that of II was unchanged, we had

$$\frac{\text{I}}{\text{II}} = 3{\cdot}01 \text{ with one element,}$$

and

$$\frac{\text{I}}{\text{II}} = 2{\cdot}81 \text{ with three elements.}$$

Hence with identical kathodes the resistances would have been in the ratios

$$\frac{\text{I}}{\text{II}} = \frac{3{\cdot}01}{1{\cdot}16} = 2{\cdot}59,$$

and

$$\frac{\text{I}}{\text{II}} = \frac{2{\cdot}81}{1{\cdot}115} = 2{\cdot}52.$$

In a medium twice as attenuated, the negative light which occurs at the same difference of pressure flows further from the kathode, and, as far as can be judged without measuring, it has twice the diameter. Its intensity appears considerably less.

From the previous discussion it follows that the ratio of the resistances of the glow-light appears much smaller when the tubes containing gas of various densities are separately introduced into the induction-current. The lengths of the capillary cylinder of the solution of zinc sulphate, which had to be introduced in order to change the intensity of the current as much as the tubes with hydrogen of the tensions 1 and ½ mm., were in the ratio 13 : 17.

25. Besides the density of the medium, two other circumstances—variations in temperature and the substance of the kathode—influence the number 2·6 for the ratio of the resistances which the glow-light has when the densities of the medium are as one and one half. The influence of the material of the kathode is distinctly recognized when two tubes identical in all respects, except as regards the metal of the kathode, are inserted abreast in the induction-current.

I have as yet made these experiments with only a small number of metals (Al, Pt, Ag, Zn, Fe) and have not concluded them. The results obtained are remarkable enough to be given here.

With the metals named there are differences by no means inconsiderable in the resistances of the glow-light, which is formed at the same difference of tension. The resistance of aluminum is the least, and is less than one fourth those of platinum and silver, which are tolerably equal, and more than two and a half smaller than that of zinc. Platinum and silver, as is well known, are amongst the metals most easily disintegrated by the negative light, while aluminum gives no deposit on the surrounding glass sides. We shall thus be inclined to seek here for the cause, and in addition to the resistance, assume with Edlund, an electromotive force due to disintegration. I must for the present leave this question open, with the remark that iron, although it gives very slight deposits, offers a somewhat greater resistance in its glow-light than silver or platinum.

The ratio of the resistances which the glow-light presents under the same circumstances at the surface of two different metals, varies somewhat with the strength of the current and the density of the gaseous medium.

26. The resistance presented by the glow-light at a particular surface, which steadily increases with the rarefaction, and which occasions the continuous decrease in the intensity of the current, may be used to replace the manometer, which at pressures of less than 0·05 mm. is useless, by the needle of the galvanometer, and thus the action of the aspirator may be controlled. The tube which serves for this purpose must have a large diameter just where it surrounds the kathode (of at least 60 mm.), in order to avoid the disturbing action of the conditions to be mentioned in the next article. The most extreme rarefaction of which the pump is capable is attained when the deflection of the needle remains constant on further letting off the mercury. This takes place also when the mercury strikes against the principal stopcock as sharply as in the Torricellian vacuum.

27. As regards its behaviour on increase of rarefaction, the negative light is in complete opposition to the positive, the resistance of which steadily decreases if the dimensions are constant. In order to arrive at this conclusion I used one of the ellipsoidal receivers in which were fused, as shown in fig. 12, Plate I., two glass tubes 13 mm. in width and of very

different lengths. These contained the similar aluminum wires *a* and *b* which served as anodes, and hence were at very different distances (the difference was 115 centim.) from the kathode *c*. The latter finally was a platinum wire which projected 73 mm. from its capillary tube, and was in the widest part.

My intention in the preparation of this apparatus will be apparent. I wished to produce two paths for the current which, as far as possible, should offer the same small negative resistance, and very great differences in the lengths of the positive light. If the induction-current is passed first through the path *ac*, and if the deflection of the needle is observed, then, when the path *bc* is substituted, it will be necessary to introduce a definite length of the solution of zinc sulphate in order to reproduce the same deflection. This, then, will have the mean resistance which the length (115 cm.) of the positive light exerts at the strength of current used.

I first of all convinced myself that the resistance of the positive light in the same medium varies with the intensity of the induction-current, and decreases when the latter increases. Thus with the current-strengths 1, 2·3, 4·9, the lengths of the capillary cylinder of solution of zinc vitriol, which replaced the positive light of 115 cm. in air of the pressure 0·05 mm., were as 61 : 34 : 23.

The most superficial observation is sufficient to see that at greater densities of the gaseous media the induction-current is mainly enfeebled by the resistance of the positive light, and the latter falls steadily with the pressure. I endeavoured to ascertain by the above means whether this behaviour holds at the high rarefactions which the aspirator can produce, or whether there is a point of inversion. Phenomena which the next paragraph will discuss lend some importance to these determinations, and induced me to extend them as far as possible.

As the details are of no interest I will only give the general result. To a pressure of about $\frac{1}{320}$ mm. (this figure is calculated from the number of times the mercury of the pump has been let off since the last determination by the manometer), the resistance of that stratum of air which radiates positive light steadily decreased, although the intensity of the induction-current which the same galvanic elements produced continually sank owing to the increase of the negative resistance. At the most extreme rarefactions which the pump produces, the two paths for the current *ac* and *bc* no longer give definitely different deflections, for the negative resistances become too great.

28. There is one phenomenon which directly manifests the opposite of the behaviour characteristic of the resistances of the positive and negative lights at decreasing pressure. This occurs when two conductors connected with each other are placed at different points in the gaseous path, and a partial current is shunted from them.

For this purpose I used the tube represented in fig. 13, Plate I., which was provided at the ends with electrodes of aluminum, and in which the two aluminum wires *m* and *n* projected 25 mm., being at a distance of 315 cm. As long as the pressure was above 1·5 mm., which of course depended on the length of the layer of gas, feeble red light occurred in the latter with broad bands. Its intensity rapidly increases as the rarefaction continues, while the negative light about *m* becomes continually paler. As long as the latter is more strongly luminous, it is separated on both sides from the positive light by dark spaces. They disappear at greater rarefaction, and a layer of red light directly surrounds the feeble blue light of *m*. The eye now recognizes no difference in the brightness of the positive lights, which fill the space *mn* and the paths *am* and *nc*.

If we determine the intensities of the shunt current in the wire *mn*, and of the total current for a given pressure, we get the ratio in which the resistances of the positive light *mn* and the glow-light about *m* stand to each other. Although the results of these measurements have an individual character, as they depend essentially on the dimensions chosen, a knowledge of them is interesting, since the rapid change of the ratio of the resistances follows directly from them. At the pressure 1·5 mm. the currents which traversed the layer of air and the wire *mn* were as 0·467 : 1. The table shows what was the ratio with increasing rarefaction.

Pressure of Air.	Intensities of the Currents.	
	In the length of Air.	In the wire *mn*.
mm.		
1·5	0·467	1
1·1	1·35	1
0·75	3·13	1
0·5	17·23	1
0·15	131	1
0·075	187·5	1

The division took place even at the most extreme rarefactions ; though the strength of the current in the wire *mn* appeared to decrease more slowly.

29. The electroscopic action of the tubes with rarefied gases is in accordance with the behaviour of the resistances of the positive and negative light. If, as Riess has done*, we investigate in this direction a tube at a pressure of the gas at which the resistance of the positive light still considerably exceeds that of the negative, we meet with the electrical conditions which he has described. The parts which are near the middle of the distance between the electrodes are unelectrified ; the column of gas is always more strongly positive towards the anode, and continuously more negative towards the kathode.

If, however, so small a tension of the gaseous medium is chosen that the resistance of the positive light is small compared with that of the negative, the tube is positively electrified throughout its entire length. The kathode itself must be touched in order to obtain a negative deflection with the Bohnenberger's electroscope.

30. The results obtained teach us that the maximum conductivity of a given gas by no means depends on the rarefaction alone, but that the dimensions of the tube and of the kathode have also a great influence†. If the kathode is large,

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* Pogg. *Ann.* vol. civ. p. 323.

† *Ibid.* vol. cxxx. p. 612.

the receiver sufficiently wide, and the distance between the electrodes considerable, the greatest deflection of the galvanometer will take place at pressures which are far below 1 mm. Thus hydrogen in tube, fig. 12, Plate I., gave the maximum deflection only at the pressure 0·15 mm., when the current took the path *ac*. In a tube with point-shaped kathode, and electrodes a small distance apart, this gas had the greatest conductivity at 5 mm.

31. When the air was gradually rarefied in the tube 60 cm. wide (fig. 2, Plate I.) with the kathode 82 cm. in length and at a distance of only 5 cm. from the anode, the deflection of the galvanometer given by the induction-current, excited by the same element, was constant with a pressure of 2·75 to 0·3 mm. During this decrease of density the glow-light gradually extended over the entire length of the negative wire, and thus, by the increase of dimensions, the increase of resistance met with when the surface remained constant was fully compensated.

If there are no points of inversion for this different behaviour of the resistances of the negative and positive lights, a kathode of any given length will be covered with glow-light in a sufficiently wide tube as the rarefaction progresses, and thus a good conductivity obtained even at the smallest density.

We are therefore far removed from the production of a vacuum which does not conduct, and the prediction of the great British philosopher, that a vacuum does not conduct, appears as if it would never be realized. It would be worth while to prepare Geissler's aspirator in large dimensions, and to continue the experiments of this article with longer and wider tubes.

§ 4.

32. The extension of the glow-light over the kathode presupposes, as I have several times had to remark, a certain density of the surrounding medium.

If, at the ordinary density of the air, two thin platinum wires, serving as electrodes for the current on opening, are at a small distance from each other, the glow-light which covers the terminal surface and several millimetres of the side of the negative pole may be got rid of on the latter by pushing over it a tightly-fitting glass tube. It is not necessary to fuse the glass over the wire, as was done by Sinsteden, to whom we owe this observation. With the disappearance of the hot glow-envelope the heating of the wire also ceases.

In his vacuum tubes, Gassiott stops the glow-light over the greater part of the kathode, and therewith the metallic deposit on the surrounding sides of the tube, by fusing about the negative wire a glass capillary tube, open in front, which has a somewhat larger diameter and projects a little.

These two are the only observations which I have met with in literature respecting the fact with which we are now to be concerned.

33. If, for a given electromotive force of induction, the glow-light is to attain its greatest extension over the length of the negative wire, which is always supposed to be in the axis of a cylindrical tube, the diameter of the latter must not have less than a certain magnitude. The width necessary increases with the rarefaction of the gaseous medium, and attains no inconsiderable dimensions with the low densities which the mercury aspirator can produce. Tubes whose diameter is less than 40 mm., and which are provided with negative wires of sufficient length, show with the Geissler's pump a maximum for the length of the glow-light. It is so much the smaller, and occurs at so much the higher pressure of the gaseous medium, the narrower is the tube. Thus, for instance, with an induction-current furnished by two elements, it was only 1·5 cm. when the thickness of the column of air around the negative wire was 1 mm.; it was 45 cm. on the other hand when the width of the tube was 32 mm.

If the exhaustion is continued, the length of the glow-light in such tubes steadily diminishes. If the diameter of the tube is less than 25 mm., the negative wire remains dark at the greatest rarefaction which the aspirator can produce without heating the gaseous medium; only from the end opposite the anode does negative light issue, which, however, seems only to begin at some distance, because the mean dark layer has acquired a considerable thickness. Its feebly luminous rays acquire a considerable extension, and pass through tubes a foot in length. The glass sides which bound it are fluorescent with a bright greenish-yellow light, and lose some transparence. Positive light cannot for the most part be seen. In such a cylindrical tube, therefore (fig. 14, Plate I.), the part which surrounds the positive wire, and the space between the electrodes, will be of a bright green, and that part at which the anode is introduced will be particularly bright, because it is opposite the end of the kathode. Any one who had not followed the changes of the negative light on progressive rarefaction, would believe that here the discharge proceeded from the foot of the anode and pursued its path over the inner surface of the glass, passing over in the neighbourhood of the kathode. The appearance of the tube is, of course, somewhat dependent on the strength of the induction. If the number of voltaic elements is increased, a green fluorescent light adds itself to that already described, as a more or less broad ring about the end of the kathode.

34. In these small tubes the wires must not be cemented in with sealing-wax, for this substance, as already remarked, is decomposed with the formation of gases, when the hot electric light strikes against it. Platinum wires must be fused in. Some kinds of glass are not suitable for this purpose. Herr Schertiger, our skilful maker of glass instruments, who helped me, could not succeed in producing a hermetical closure with difficultly fusible potash glass; and Dr. Geissler has communicated to me the same fact. Platinum always separates from this kind of glass, which softens on expansion, and air slowly enters through the fine slits. Schertiger surrounds the platinum wire in the place where it is to be inserted with easily fusible lead glass, and fuses it into the glass of the tube, which is obtained from a manufactory in Thüringen.

35. After the foregoing discussions it follows that such a tube, in which the negative light at the high rarefaction has been reduced to so small a surface, must offer an extremely high resistance to the current, and that this resistance will be independent of the distance between the electrodes. The projecting wires show indeed high electrical tensions, and give large sparks even when they almost touch in the interior. In order to estimate the rarefaction, the galvanometer may be replaced by the spark-micrometer, which is to be interposed in a second

circuit. That which I used had bulbs of 2·75 cm. diameter. The induction-currents can thus traverse either the air-space between the latter, or the rare medium of the tube.

If the aspirator is provided with fresh non-deliquescent phosphoric acid, and if the letting off of the mercury is continued until it strikes sharply on rising, tubes whose diameter may reach 20 mm. can be obtained, in which the discharge only takes place when the bulbs of the spark-micrometer are at a distance of 30 mm. If the latter distance is much smaller, the tube remains quite dark. A very feeble green fluorescence occurs simultaneously with the spark in the micrometer only on coming near that limit.

If the circuit with the exhausted tube contains also an ordinary Geissler's tube, with air of 1 to 2 mm. pressure, there is seen in the latter, as Gassiott has already noticed, an extremely feeble glow-light at both electrodes when the discharge takes place in the micrometer. That path is then traversed by alternating flashes of small intensity. If the discharge occurs in the vacuum-tube Geissler's tube has a brighter light, in which the stratification and the dark space are wanting. It is uniformly red all over, and agrees with that which is produced by introducing a longer air-break, as well as with that produced by the current of a Leyden jar*.

The exhausted tubes at these pressures not only insulate Ruhmkorff's coil, but also a charged Leyden jar.

36. The tubes which are to show this resistance, after having been exhausted, remain for some time in connexion with the pump before being fused, so that the phosphoric acid may exert its full action.

The highest degree of exhaustion is obtained by simultaneous strong heating. For this purpose I used the vapour of boiling sulphur (447° C.) or of phosphorous pentasulphide (530° C.).

The tube, as shown in figure 15, Plate I., is enclosed within a closely-fitting thin glass cylinder, fused at the bottom, about which the vapours rise in the wide vessel. Direct contact is not permitted, for the platinum would be attacked. The tube by which connexion is established with the air-pump is narrowed at the place which is to be fused, and is surrounded with a platinum wire, on the ends of which are binding-screws. At the moment of fusion, the latter are connected with a suitable voltaic couple. The platinum wire becomes incandescent, and the glass in the loop fuses.

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* The conditions described in this communication do not hold for the discharge of a Leyden jar.

For convenience in heating these tubes their length is only from 5 to 6 cm. They do not transmit the strongest induction-current, for it takes the path through the air over the outer surface, and passes here as a spark. To prevent this, I place the small glass tube in another which is wider and much longer (fig. 16, Plate I.), and fill the interstitial space with a denser insulating medium, such as oil of turpentine. The connexion with the exterior is effected by means of wires.

I have thus several times prepared tubes whose diameter was as much as 15 mm., that do not transmit the strongest current of my Ruhmkorff's coil, which gives a spark in air of 16 cm.

Their durability is considerably restricted by a circumstance which may fortunately be diminished. The tubes prepared in the factory by drawing out have always longitudinal striæ, which are extremely narrow channels filled with gas, and which result from the gas bubbles in the melted glass. If they are in the sides of the exhausted little tube, alternating currents are induced in their enclosed gas by the high electrical tension, and the channels usually crack at the sharp drawn-out ends. The cracks then allow air or the oil of turpentine to enter. At first I lost many a tube in this way with the first powerful discharges of the Ruhmkorff coil. By suitable softening at the lamp, however, the longitudinal slits may be got rid of; this must, of course, be done before proceeding with the construction of the tube *.

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* Wullner's notice (Pogg. *Ann.* vol. cxxxiii. 1868, p. 509) reports on these tubes. I showed them in the autumn of 1865 to Geissler in Bonn, who endeavoured since that time to reproduce them as a testimony to the excellency of his aspirator. Plücker, to whom I presented several, took them to Gassiot on his journey to England, who was also astonished at the high tensions, which are far superior to those of his carbonic acid vacuum. In the spring of 1867, Plücker exhibited them in Paris. During the Exhibition, in September of that year, I was enabled, by the kindness of Ruhmkorff, to use one of his largest coils, which gave a spark of 40 cm., and to make some experiments in his workshop, to which I shal afterwards revert. I left with him at that time my store of uninjured tubes.

37. That the resistance of these tubes depends on the small dimensions as well as on the rarefaction, may be very easily shown by surrounding one of the equal wires with a narrow tube and the other with as wide a tube as possible, as shown in fig. 17, Plate I. A glass flask of 8 to 10 cm. diameter is well suited for the preparation of such a receiver. On sufficient rarefaction the difference in the distances of the micrometer at which the discharge takes place in one or the other direction becomes very striking, and may amount to twenty times as much one way as the other. If the wire in the wide flask is negative, it is covered over its entire length with feebly luminous glow-light, which flows over to the sides of the glass, and excites bright fluorescence. The dark space separates it from the positive light. If there is an ordinary Geissler's tube in the circuit in addition to the flask, the same three parts are met with here. If, however, the wire of the narrow tube serves as kathode, the glow-rays proceed as a conical bundle from the end only, flow through the space of the bulb, and produce on the opposite side a bright fluorescent circle which has the entrance of the anode for its centre. Light produced by the discharge of a Leyden jar occurs in the Geissler's tube of the circuit.

38. The results of the foregoing paragraphs contain directly the explanation of the high resistances which the evacuated tubes show, when we know the cause which prevents the formation of the glow-light on the whole surface of the kathode.

We should be first of all inclined to consider that the width of the gaseous medium is not sufficient for the full development of the glow-light, since for the same density its rays acquire a far greater length in a wide tube than in a narrow one. But a slight modification of the tube shows that the reason is not to be found here.

For if (fig. 18, Plate I.) the end of the wire is in the axis of a narrow tube, and the other part in as wide a one as possible, for the same degree of rarefaction the behaviour of the glow and the resistance are the same as in the tube which for its whole length has that small width. The negative light proceeds likewise only from the end of the kathode, and floods the anode. The whole of the rest of the kathode, even where it is surrounded by the wide tube, remains dark.

If the above assumption be correct, the glow-light must be developed on this path, and the narrow tube, if its width is insufficient for the production of the glow-light, must be filled with positive light. The latter takes place at the greatest rarefactions, even in long capillary tubes, without producing excessive resistance.

In order to prevent the glow upon the length of the negative wire it is not even necessary that there be a great length in a narrow tube. It is sufficient only if its end is near enough to the mouth of the narrow tube.

In the vessel (fig. 1, Plate II.) which consists of two wide bulbs, connected by a narrow tube, this condition is fulfilled for the wire *e*, while the wire *a* is still far from the mouth. If the former is the kathode, no negative light appears in the bulb surrounding it at a sufficient rarefaction, but a brush proceeds through the narrow tube to the place where the wire *a* enters, and produces there a small circular fluorescent spot. When the current is in the opposite direction the wire *a* is totally covered with glow-light, and the surrounding sides fluoresce. The resistance is, of course, much smaller than in the first case.

39. We shall be led towards a correct interpretation of our facts, if we notice a phenomenon which always occurs when the glow-light has obtained its maximum extension, and which so far has not been mentioned. It is best seen with air or nitrogen, and in narrower tubes in which, even at a greater density, the extension of the glow-light finds a limit. If this latter has been met with, the mean dark transparent layer of the glow-light fills up the width of the tube, and the outermost, strongly luminous layer is no longer perceived. In its place there is a reddish-yellow positive light, which is not infrequently stratified. It occurs close to the glass side, over the entire length of the wire covered with glow-light, and has only a slight thickness. If the wire is not exactly in the axis of the tube, it forms a reddish-yellow band on that side of the wire which is at the greatest distance from the glass.

If this positive light forms over the kathode at greater rarefactions in wider tubes, the colour is paler and is at length white, like that of the positive light generally.

The other gases behave in exactly the same manner as air and nitrogen, with the exception that, in the former, the difference in colour of the two lights disappears.

40. The phenomenon is perceived also in the wide vessel (fig. 18, Plate I.). If the diameter and length of the narrow tube are suitably chosen, as the density diminishes, the glow-light extends just over the whole of the negative wire *c*, and fills the wide tube completely. If then, as the exhaustion proceeds, the dark mean layer has occupied the diameter of the narrow tube, the positive light appears over it, and runs over the mouth of the wide vessel into the extreme layer there. At the same time the dark space, which existed in front of the end of the kathode, disappears, for the positive light from the anode passes uninterruptedly into that which appears over the kathode. If there is only a small change of density, the glow-light which filled the wide tube is wanting. The narrow channel also is soon dark, and the negative light withdraws to the end of the kathode. In the tube (fig. 1, Plate II.) the occurrence of the positive light at the mouth of the narrow tube, and the disappearance of the dark space, precede the cessation of the glow-light on the length of the wire *c*.

41. If in the tube (fig. 18, Plate I.) the two parts of the negative wire in the narrow and the wide tube are separated, so that, as shown in fig. 2, Plate II., the connexion outside the tube can be made and broken at will, the hindrance to the spread of the glow is directly perceptible. For if the wire *c′* in the narrow tube is disconnnected from the kathode, then, whether it is isolated, or is in connexion with the earth, the positive light at each high degree of exhaustion is formed near it, and extends as far as the opening of the wide tube. Here is the dark space, and the entire wire *c* is surrounded by negative light. If the length of *c* is taken sufficiently great, the resistance at the extreme rarefaction may be made sufficiently small, so that with a micrometric distance of 1 to 2 mm. the spark no longer appears.

When, however, the wires *c* and *c′* are connected, the positive light in the neighbourhood of the former disappears; a brush of negative light, producing fluorescence, proceeds from its end opposite the anode, and the part *c* is dark.

If while *c′* was still disconnected from *c*, and the knobs of the micrometer in the lateral branch were so far apart that no spark passed here, then, when the length of the kathode was increased by c', the increased resistance manifested itself by a stream of sparks. The knobs must be separated by 20 to 30 mm. if the induction-current is still to choose the tube. It is a matter of course that a galvanometer interposed in the wire *cm* experiences no deflection, and the piece *c* takes up no part of the current when its glow-light has completely disappeared.

42. Experiment, therefore, renders apparent what indeed is already clear from the observations of the foregoing paragraph, that all the rays of the glow-light which proceed from the particles of the negative surface endeavour to join the positive light. If this is not possible, the glow ceases. Under ordinary circumstances the eye cannot recognize this combination, since the positive current passes principally through the extreme luminous layer of the glow-light, but develops no light owing to its small density and resistance. If, however, it is concentrated in the narrow tube on the thin layer, the gaseous particles must again become luminous with its light.

The second conclusion could not be foreseen. The positive light, which in the rarefied gaseous medium only slightly enfeebles the current, and then fills capillary tubes even with comparatively small resistances, finds great difficulties for its formation in the vicinity of the kathode. The hindrances exist in the wider area about it, the more rarefied is the medium.

43. More light is thrown upon this by measurements of the resistance offered by kathodes to the current when they are surrounded by tubes of different widths, but identical in all other respects. A glance at fig. 3, Plate II., shows at once what arrangement was made for these determinations. The diameter of the tube *ac* was 46 mm. for the whole length; the tube $a'c'$, which was interposed in parallel with the other, consisted of a piece of 46 mm. diameter for the anode, and 12 mm. diameter for the kathode. The respective electrodes are of the same length and thickness in the two tubes, and the same distance separates the ends. Apart from small inequalities of the surfaces, which have been previously discussed, the induction-current divided itself equally between the two tubes at those densities at which both kathodes became wholly coated with blue glow-light. The same division also took place when the glow-light in the wide tube filled the entire diameter, and

when, therefore, its rays had far greater length than that of the narrow tube. It continued even when the reddish-yellow positive light had made its appearance in the narrow tube. But as the negative light shortened, the intensity of the current rapidly diminished as the rarefaction proceeded. In this tube of 12 mm. diameter, the positive light occurred first at a tension of 0·375 mm.

44. The result which these measurements of the intensities of the current give, may be made at once accessible to observation by another form of the tube.

In the receiver represented in fig. 4, Plate II., the two aluminum wires, *a* and *c*, which serve as electrodes, are partially surrounded by a wide and partially by a narrow tube. The ends in the latter were only at a distance of 1 mm. apart. The wide vessels were connected by a second tube *n*, which was as narrow as the first but much longer.

If the air in this system is gradually rarefied, the induction-current at first uses only the short tube *m*. The long one, *n*, remains still dark at a density at which the reddish-yellow positive light had already appeared in the narrow tube *m*. The pressure of the gas needs now only a slight diminution for the induction-current to divide between the tubes *m* and *n*, filling the latter with a feeble light. As the exhaustion proceeds the luminosity of the channel *n* rapidly increases at the expense of that of *m*, and at length this latter remains quite dark.

The glow-light in the wide tube, of course, does not disappear, and hence the resistance of the system continues to be small. If, however, a glass stopcock is introduced into the channel *n*, a great resistance can be produced by closing it, and luminous phenomena be obtained, which are sufficiently discussed in the accounts of the other tubes.

45. The obstacle which the vicinity of the kathode offers to the formation of the positive light comes into play also in wide tubes. In a bulb of 10 cm. diameter (fig. 5, Pl. II.) there were two parallel aluminum wires, *a* and *c*, at a distance of 4 mm. apart. As the two narrow tubes in which the capillary tubes were inserted could not be fused sufficiently close to allow of this, the wires where they came out of the capillaries were slightly bent so that they were at that small distance.

If these wires are used as electrodes with great rarefaction of the air, the glow-light of the kathode floods the whole bulb and produces a bright greenish-yellow fluorescence on the sides. The white positive light does not follow the shortest path to the kathode, but appears on that side of the wire away from the negative, and receding from the latter flows along the sides of the tube to the extreme layer of the glow-light. Indeed, when the rarefaction was carried as far the pump allowed, not only the space between the electrodes but the entire length of the anode parallel with the negative wire remained dark, and only on the bend where the distance from the kathode is greatest was there a white flame flowing towards the sides.

46. The phenomenon becomes still more striking if the free surface of the positive wire is surrounded by a capillary tube so that only its cross section is free, and this is fixed at the small distance of 1 to 4 mm. from the long negative wire *c* (fig. 6, Plate II.).

At great rarefactions the white positive light now appears only at the edge of the section, and bends away from the latter, almost in the plane which passes through the positive wire, and is at right angles to the kathode. In this manner it reaches greater distances by the shortest path, and has just the appearance of having been blown from the kathode to the sides of the flask. The glow-light occurs most strongly in that plane in which the positive light preferably spreads out. The fluorescence of the glass is here much more intense, and stands out from the environment as a strongly luminous ring.

If the positive section is at a greater distance from the kathode (15 mm.), the positive light appears over its whole surface, flows for a few millimetres towards the kathode, and bends back from there in all directions to the extreme layer of the glow-light. Hence here the whole side fluoresces uniformly, and the ring is absent.

The smaller the distance of the positive section from the kathode, the greater does the resistance appear to be, which, notwithstanding the long kathode covered with glow-light, is not inconsiderable. Thus with the small distance of 2 mm. and the greatest exhaustion, the distance between the knobs of the micrometer had to be over 12 mm. in order that no spark should be formed. On the other hand, under the same conditions, a separation of $3\frac{1}{2}$ mm. only was necessary in order that the induction-current should discharge itself entirely through the bulb with a distance of 15 mm. between the micrometer-knobs.

47. The narrow tubes (figs. 15 and 16, Plate I.), exhausted as completely as possible, and with electrodes 1 to 2 mm. apart, show, when a strong induction-current forces its way, besides the negative fluorescent light on the extreme end of the *anode*, described above, a luminous envelope from which a beautiful mirror of finely divided firmly adherent platinum deposits on the glass. If the tube transmits the current for some time the end appears eaten away. It also becomes heated, and wires of the thickness of 0·5 mm. become feebly incandescent. The disintegration and the ignition are most easily obtained when a carbon point forms the end of the anode.

The thermal phenomena are accordingly completely reversed, as in the experiments of Gassiott (Pogg. *Ann.* vol. cxix. p. 131). The kathode, which, covered with glow-light, becomes strongly heated and pulverized, remains now quite cold and completely unaltered.

The volatilized platinum of the anode does not go to the neighbouring anode, but to the opposite side, because it, like the positive light, strives to combine with the glow-rays.

Since the best exhausted tubes, as stated above, no longer discharged my induction-coil, I took advantage of the opportunity during my visit to Paris, and subjected them to a current which gave a spark in air 40 cm. in length between the wires of the discharger. In one of these tubes the current passed after the wires of the discharger in the branch circuit were at a distance of 25 cm. The positive wire ignited at the extreme end so powerfully that it at once melted, forming a bead. The disintegration of the platinum, however, was less considerable.

With the electrodes at greater distances I never obtained incandescence and pulverization of the anode in this little tube.

48. The systems of tubes (fig. 18, Plate I., figs. 1, 2, and 4, Plate II.) may be used to throw further light on the circumstances which prevent the occurrence of positive light near the kathode. They furnish an answer to the obvious

question, as to the connexion between this obstacle and the glow-light which is actually there.

If the occurrence of positive light is made more difficult by the glow-light, then, after the removal of the latter, the former must reappear near the wire in question. The glow-light may be easily removed by preventing the entrance of the current into this part of the kathode by an insulator. When in the tubes (fig. 18, Plate I., figs. 1 and 4, Plate II.) the negative wire *c*, in so far as it lay in and near the narrow channel, was surrounded with a thick capillary tube fused at one end, the obstacles in the way of the formation of the positive light remained without change.

The system of tubes (fig. 4, Plate II.), which contain a second quite similar but entirely bare wire *a*, is most instructive for our purpose. At the same rarefaction the current begins to traverse the long channel *n*, whether the bare wire, or that partially covered, serve as kathode. By this it is proved that the hindrance to the formation of the positive light is in no sense due to the glow-light, but exists independently of it in the vicinity of the kathode. In the tubes (fig. 18, Plate I., and fig. 1, Plate II.) in which no second path is opened to the current the electrical tensions become considerable, and the glass surrounding the anode is, as Poggendorff has also recently stated *, no longer a perfect insulator. It conducts to some extent, and becomes covered with a faint envelope of glow-light which excites fluorescence. At a definite electrical tension, which depends on its thickness, it is perforated by a spark near the end of the kathode. If the wire c' (fig. 2, Pl. II.) is entirely coated with glass over that part which is within the tube, by introducing the galvanometer into the circuit $c'm$, it can be seen how inconsiderable the current is which passes through the glass envelope into the kathode.

This tube is well adapted for demonstrating the influence of the kathode. If the galvanometer is introduced into the circuit *cm*, or if a shunt circuit with a spark-micrometer is added, great differences are met with in the deflection of the needle and the tensions, according as the wire c' coated with glass is in conducting communication with the bare wire *c* or not.

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* Pogg. *Ann.* vol. cxxxiv. p. 304.

In the wide receiver (fig. 5, Plate II.) also it may be shown that the kathode exerts an influence which is unfavourable to the formation of the positive light independently of the glow-light. For this purpose wires, as shown in fig. 7, Plate II., were placed in the ellipsoid, the small axis of which is 10 cm. The bent wire *a* served as kathode, and was fixed parallel with and at the small distance of 4 mm. from *c'*, which was entirely surrunded by glass, while *c* formed the anode. When at the most extreme exhaustion *c'* was put in conducting communication with *c*, the positive light disappeared from the length of the wire *a*, and withdrew to the most distant part of the bend *m*, although it had the greatest distance from the glow-light at *c*.

§ 5.

49. The experiments of the foregoing paragraph led to the conclusion that special conditions exist in the neighbourhood of the kathode which do not allow of the propagation of electricity in the same manner in which it takes place in the positive light, and prevent this current from entering the negative surface. It must therefore be supposed that the conduction there is due to the glow.

As a matter of fact the rays of negative light as regards their deportment towards the magnet, which we shall now examine, behave like simple currents, that, as far as direction is concerned, flow from the neighbourhood into the kathode.

50. According to the law which Laplace deduced from the experiments of Biot and Savart, a pair of forces are at work between each particle of a linear current and the pole of an infinitely thin magnet, which are at right angles to the parts of the current and the pole, and whose intensity is inversely as the square of the distance between them, as well as directly proportional to the sine of the angle which the particles of the current form with its connecting line with the poles. Since, for a finite magnet, the tangent to the magnetic curve which passes through the particle of the current represents the direction towards the pole, the force acting on the element of the current is at right angles to the plane which passes through it and the magnetic curve of its locus. Ampère's rule defines which of the two directions of

these perpendiculars holds in a given case. For an observer swimming with the current along the tangent to the magnetic curve and looking at the pole, the element of the current is driven to the right when it is north magnetic, and to the left when it is south magnetic.

51. In order to produce the simplest conditions for the glow-light, we used a pencil of approximately parallel rays, such as is formed on the section of a wire which is surrounded for its entire length with a small glass tube (No. 10). It is advantageous to take the diameter of the wire not too small (1·5 to 3 mm.) and the rarefaction of the air slight (·25 to ·125 mm.). The pencil of rays is then very distinct, extends for a length of several feet, and wherever it strikes against the glass it evokes bright greenish-yellow fluorescence which facilitates observation. In order that in all directions it may freely follow the action of the magnet, the thickness of the glass must be small and the wire project some distance in the receiver. A cylindrical tube 30 to 40 cm. in length and 45 to 50 mm. in width (fig. 8. Plate II.), and a glass bulb of 6 to 10 cm. diameter (fig. 9, Plate II.) are very suitable vessels.

The electromagnet used consisted of two iron cylinders, 10 cm. in diameter and 50 cm. in length, surrounded by coils of wire, which were connected by a square iron bar 10 cm. in the side. In order to change at pleasure the strength of the magnetism a rheostat was introduced into the current which produced it. For this purpose a cylinder filled with a solution of zinc sulphate and dilute sulphuric acid was used, whose terminals were two amalgamated zinc plates of 9 cm. diameter, and whose length and resistance could be changed at pleasure by raising or sinking a plate.

52. Laplace's law, which governs all currents, holds in the same way for positive as for negative light. So long as the magnet is feeble, the movements which both perform in the cylindrical tube appear almost the same; they are, however, different the stronger is the magnetization.

For the glow-ray behaves like an infinitely thin rectilinear imponderable stiff thread of current which is only fixed at the end touching the negative section. At its other end and throughout its entire flexible length, it obeys the forces between its particles and the magnet, without reference to the position which it has in respect of the anode, or whether it moves away from or approaches it. The positive light maintains the connexion between the glow-rays, in the position which they each time take up, and the anode, and is suited for this by the small resistance which it possesses in the highly rarefied media. Hence it appears as a conductor flexible throughout its entire length, both of whose ends are fixed, and it can only obey magnetic forces in so far as it satisfies this condition.

Holding to this distinction, the forms which the bundle of parallel rays assumes in the various positions of the magnet seem intelligible.

53. Let only one pole act upon the current, one only of the two limbs of the electromagnet being used.

Let the cylindrical tube lie with its axis parallel to the plane terminal surface. Let the latter be north magnetic, and first of all be feebly excited by introducing the whole length of the rheostat.

The negative pencil, which keeps in the axis of the tube and floods the anode so that the positive light is invisible, bends to the right of an observer, supposed to be swimming towards the kathode and looking at the north pole. The anode is thereby free and the positive light is seen to be turned towards the same side in the interstitial space, in which are no glow-rays.

If the strength of the magnet is increased by gradually shortening the rheostat, the curvature of the glow-light towards the right increases, and windings are formed which lie on the right of the section, and are continually narrower. At the same time the positive light extends, and follows the retreating negative on the right side of the tube.

In order to produce all the shapes which the glow-rays can assume in this magnetic field, the bulb-shaped vessel, fig. 9, Plate II., is more convenient, since the axis of the pencil of light in it can take any position in reference to the magnetic surface without the distance of the section changing. If this axis is at right angles to the magnetic curve passing through the negative section, the glow-rays, which have the direction of the former, alter with a sufficiently powerful magnet into a plane circular coil which is at right angles to the magnetic curve. On both sides of it the diverging rays lie affixed as spirals. There is thus formed right of the section a beautiful cone which is most strongly luminous in the centre, and the section of which diminishes continuously as it gets nearer the polar surface, since the force of curvature increases here.

If the section is over the centre of the pole surface, where the magnetic curve is vertical, the cone also stands vertical (fig. 10, Plate II.).

If the magnetic curve which passes through the negative section forms with the axis of the luminous pencil an angle differing from a right one, the rays parallel with the latter pass into a curve of double curvature, a spiral, the windings of which are so much the narrower the nearer they are to the poles. Hence they lie again on the surface of a cone the apex of which is turned to the pole. Two or three complete windings can be readily distinguished. Where they strike against the glass side they excite bright fluorescence ; they are not stopped by the glass, but prolong their curves over it. One part of the rays winds backwards about the magnetic curve of this place, and only finds a limit to its further extension in the opposite side. The appearance presented by these windings as the rheostat is gradually shortened is most beautiful.

Although each particle of the current is defined by that magnetic curve which passes through its locus, its direction is essentially defined by that of the adjacent particle which lies nearer the negative section. It hence arises that with increasing magnetization the axis of the spiral continually approaches the same magnetic curve, namely, that which goes through the point-shaped kathode.

The spiral turns away from the magnetic pole if the angle, which the direction of the current forms with the tangent to the magnetic curve of the section, is obtuse (fig. 11, Plate II.). It turns towards the pole when the angle is acute (fig. 12, Plate II.). The more it deviates from a right angle the greater, for the same strength of magnetic force, will be the height of the individual windings. If, lastly, the magnetic curve coincides everywhere with the axis of the pencil, the direction of the parallel rays is unchanged when the magnet is excited. Only the diverging rays wind about the axis, and the section of the pencil diminishes. This is very beautifully seen if the axis of the luminous pencil is at right angles to the centre of the pole, and the rays flow towards it. As the strength of the magnet increases, the great fluorescent circle which they produce becomes almost reduced to its centre, which thus becomes strongly luminous and heated. With a somewhat powerful induction-current the glass melts here on the surface, and partially volatilizes, as shown by the occurrence of the yellow sodium light. The experiment must be stopped if the vessel is not to be destroyed.

The induction-current traverses all the windings, which the glow-rays form under the action of the magnet, always in the direction opposite that of the molecular currents of the magnet, and of the voltaic current in the coil. Hence the spiral would magnetize an enclosed iron bar in the opposite direction to the given pole.

It is a matter of course that the glow-rays coil towards the left side of the swimmer; that all other phenomena are, however, the same, if a south pole is used instead of a north pole.

54. The behaviour of the negative pencil when exposed to the action of two poles may also be easily interpreted. If they are of the same kind and strength, and if further the axis of the pencil is in the equatorial plane, equal and opposite forces will be exerted on the parallel rays, which therefore must neutralize each other. It is scarcely possible to realize this condition in the experiment. One pole has always a slight preponderance, and produces a slight deflection. To this must be added that the particles of the rays which diverge from the axis are at different distances from the two poles, and must therefore undergo a slight bending. The action of the magnets can therefore never altogether vanish, but it is so small that it may undoubtedly be regarded as the difference of two approximately equal exertions of force.

If the two poles are opposite, their actions superpose themselves. As at the same time the magnetization occurs more strongly in the cylinders connected by the external crosspiece, and provided with armatures, the windings of the glow-rays will be much narrower on using the same voltaic current than when only one pole is used.

If the axis of the negative pencil lies in the equatorial plane, then, for a swimmer looking at the north pole, the rays parallel with it bend to the right at the section in a circular winding, which again is at right angles to the magnetic curve of its centre. At the same time the spirals of the diverging rays lie against it. When a strong galvanic current is used, the luminous cylinder which is thus formed has a diameter less than 1 mm., and therefore coincides almost with the magnetic curve passing through the point-shaped kathode (fig. 13, Plate II.). If the strong current is closed without using a rheostat, the magnet attains its greatest power in so short a time that the eye cannot follow the rapid movements of the light which are the conditions for the formation of the cylinder. The glow-rays appear then to have passed into the magnetic curve of their starting point.

If the axis of the negative pencil is axial and coincides with the line connecting the poles, the direction of the parallel rays remains unchanged when the magnetism is excited. The diverging rays alone rotate, forming a cylinder of almost infinitely small diameter about them.

The phenomenon is most beautiful when the cylindrical tube is in the axial position on the armatures, so that the magnetic curve of the section forms an acute angle with the axis of the pencil. The glow-rays now coil, forming a long drawn-out spiral which curves over the space between the pole-pieces as a beautifully luminous arc. It is seen distinctly, even with a strong voltaic current, that the axis still diverges from the magnetic curve which passes through the point-shaped kathode. If, for instance, the latter lies upon the armature of the north pole, the beginning of the arc is on the right side; but its end over the armature of the south pole is on the left of the axial plane which passes through the negative section. If the glow-rays are sufficiently long they do not end where that arc strikes against the glass. They partially bend backwards about the magnetic curve of this place, and produce a second similar feebly luminous arc, which forms an acute angle with the first, and terminates still more to the left of the axial plane which passes through the negative section (fig. 14, Plate II.). This second arc forms also in the case of fig. 13 from the diverging rays, and is the cause why the cylinder on the left is not sharply defined.

That part of the glass on which both arcs strike (fig. 14) is so powerfully heated that it melts on the surface, and partially volatilizes. The spiral lines into which the glow-rays run are thereby fixed.

While the negative light forms several spirals in the axial direction, the positive in this position can at most form a long drawn-out one, the height of which is the distance of the anode from the windings of the glow-light *.

55. After having studied the magnetic behaviour of the individual glow-rays, and of their pencil proceeding from the same point, we can directly explain the splendid luminous surfaces which arise with a powerfully excited magnet from the glow-light of an extended surface, and the knowledge of which we owe to Plücker. We need only remember that the force which, in accordance with Laplace's law, acts on the particles of the current, displaces the pencil from the starting-point when sufficiently strong, and may withdraw the glow-light from entire places on the surface.

If, for instance, in a cylindrical tube (fig. 15, Plate II.) the kathode has a cylindrical disc, and if this is quite coated on both sides with glow-light, it is made dark in the position in which its plane lies axially between the poles, with the exception of the highest point on the side turned away from the anode, or of the lowest on the side turned towards it, according as the displacement of the glow-rays is in one direction or the other.

In order to interpret completely the magnetic surfaces described by Plücker, which occur on wire-shaped kathodes, a metal cylinder of larger diameter (1 cm. and more) fixed as negative pole over the magnet must be observed. When this lies with its axis in the equatorial plane, its surface on and near the line of intersection with that plane will be free from glow-light, as the electromagnetic forces displace the rays in the direction of the axis.

I consider it unnecessary to go into further details, as the

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* In last spring only the train of thought of the last paragraph led me to a thorough examination of the magnetic deportment of the glow-light. The discoverer, Plücker, in his last papers (Pogg. *Ann.* vol. cxvi. p. 45), conceived the negative rays as alternating currents, and believed that, in contradiction of electromagnetic laws, they coincided with the magnetic curves. The illness and unexpected death of my honoured teacher prevented me from bringing before him the above series of experiments.

forms of the glow-light for each given surface and position with regard to the magnet may be easily explained from the deportment of the individual pencils. When the rays have a great length, careful observation shows frequent divergence from those surfaces which would be formed if the rays followed the magnetic curves, and recognizes them as necessary consequences of Laplace's law.

The changes of the glow-light due to the magnet must be accompanied by changes of resistance; these can be best recognized by the method used in § 3. Near the tube exposed to the magnet a second entirely similar one, detached from the former, is to be introduced into the induction-current, and the branching of the latter is to be determined.

56. If in the cylindrical tube (fig. 8, Plate II.) the wire-shaped anode reaches to the neighbourhood of the point-shaped kathode, the former may be allowed to coincide with the arc which the negative luminous pencil forms in the axial position above the magnet. The arc undergoes no change thereby; it encircles the positive wire, which in this position is surrounded with reddish-yellow light, and extends on the other side in the same way as if there had been no contact. Hence this fact teaches still more distinctly than that given in No. 11, that the propagation of electricity to the anode cannot take place by the process of the negative light. For this the process alone is suited which forms the essence of the positive light, and everywhere effects the combination of the anode with the currents of the individual glow-rays. But the latter find near the positive pole no such hindrance as is offered to the positive light at the kathode. The pencil of glow-rays which issues from the negative section may even by the magnet be coiled about the positive wire without disturbance. It is merely necessary in the bulb-shaped receiver (fig. 16, Plate II.) to place obliquely in front of the point-shaped kathode *c* the rather stout positive wire *a*, and to bring the axis of the negative pencil into the equatorial plane.

§ 6.

57. After the rays of the negative light have by their magnetic properties revealed themselves as simple currents

which take the direction to the kathode, it can no longer be doubted that in gaseous media the propagation of electricity takes place in a two-fold manner. One, which comes into play in the positive light, is analogous to the process which we meet with in the conduction of metals and electrolytes. The second, on the contrary, which causes the glow-light, belongs especially to the gases, and deserves greater consideration than has hitherto been paid to it. In it the particles of the negative surface are the starting-points of a motion which propagates itself uniformly as rays in all directions in the gaseous medium, and agrees therein with wave-motion. It will be a matter of experiment in the first place to compare the two kinds of propagation in as many directions as possible, and to investigate the conditions for the glow-light. This will give the conditions under which it occurs, and the reason why it replaces ordinary conduction at the kathode. If I do not deceive myself, these comparisons are peculiarly favourable for forming conclusions as to the nature of the electrical current itself; it is not impossible that, as with the theory of heat, gases will enable us to recognize most easily the essence of phenomena, and will liberate modern physics from the last of the imponderables, the electrical one.

58. If the cause of the enigmatical enfeeblement which the discharge undergoes near the kathode were called resistance, this would establish the agreement which in § 3 was observed between its deportment and that of the ordinary conductor in the path of the current. In this, however, we must recognize the essential difference, that in the gas the same particles offer such very different resistances, according as they are on the positive or negative electrode, a fact for which there is no analogy either in metals or electrolytes. That cause will both prevent the approximation of the positive light at the kathode and produce the new propagation by the glow-light.

The induction-current is not adapted for a more accurate quantitative determination of the enfeeblement which occurs at the kathode, however indispensable its services otherwise are. For, according to the different velocities with which the induced electricity flows away, the tension along the path of the current and the thermal relations of the gaseous particles will change every minute. The conductivity of the latter, however, is dependent in a far higher degree on the temperature than is that of metals and electrolytes. If we are to make determinations of resistance we must use such feeble currents that the temperature of the medium is not appreciably changed, and must by other means reach that level by which the conduction can be recognized in our galvanometers.

It is easy to formulate this requirement, but difficult or even impossible to realize it completely. For gases only begin to lose their insulation for our more accurate measuring-instruments at a red heat, a limit at which our means of maintaining a constant temperature are very restricted. The greatest drawback, however, lies in the fact that in those conditions of heat in which gases conduct, all other bodies that we know behave similarly, and no solid insulators exist. We cannot, therefore, restrict the current to a definite geometrically simple path in the gaseous medium, and in these measurements we shall remain far from that accuracy which can be obtained with metals.

This view must not, however, lead us to neglect the subject. Even somewhat less delicate determinations may reveal facts of fundamental importance, and crude approximations, provided they are correct, may be of the greatest interest.

59. Two courses may be taken to obtain gases at that high temperature; they may either be made to combine chemically with each other, or separated in a vessel they may merely be subjected to the heat developed by this process.

The use of the gases of flames itself is most convenient, and has been used for electrical purposes since the earliest times. It has the additional advantage over the other method that the heated column of gas is enclosed by an insulator of cold air, while in the former case the vessel furnishes a better conductor than the contents itself.

But the drawbacks so decidedly preponderate, and for our purposes are so great, that we should never choose flames if the manipulation in the other method did not present such difficulties.

In each flame we have to do with at least three different gases, the two which are combining, and the product of combustion, which are contained in the various parts in varying quantity. This difference in composition is accompanied by a similar one in the temperature, so that uniformity of the medium can be assumed to exist in only small spaces of the flame.

In the last few years our chemical knowledge of flames has made essential progress through the labours of Bunsen and Deville, and to the former we are indebted for the excellent gas-flame which is now introduced into all laboratories.

So far as I am aware, the experiments on electrical conductivity were all made with the flames previously in use, and which had a much less homogeneous mass than the feebly luminous cone of the Bunsen.

The most important of these investigations belongs to the beginning of our century, and in its time created great sensation. I mean the research of P. Erman, who discovered the positive unipolarity of flame, a property which stands in the closest connexion with the glow-light of our tubes. If into the insulated spirit-flame the pole wires of a voltaic pile, also insulated, which are provided with gold leaves, are brought a divergence of the latter is maintained. If the flame is connected to earth by a conductor, only the gold leaves of the positive wire collapse, and become unelectrified, while the divergence of the negative increases. This fact was met with in the case of all flames which Erman investigated, with the exception of that of sulphur, which did not conduct at all, and the flame of phosphorus, in regard to which he considered he had observed the collapse of the gold leaves, though not with complete certainty. The discoverer put this deportment of flame, erroneously, as a parallel to that of a few electrolytic substances like dry soap, which are seen to be negatively unipolar, but which owe this property to the constituent liberated at the positive pole by decomposition.

Ohm, who demonstrated the latter, did not further enter on the unipolarity of flame.

Hankel was the first who subjected this to a complete investigation*. He showed on a spirit-flame, with the aid of an electrometer, that between the negative wire and its gaseous envelope there was a considerable difference of tension, which in one case amounted to 0·87 of that of the galvanic element used, and which diminished with increase of the negative surface. The considerable resistance, which is thereby indicated at the kathode, is seen also, as Becquerel found, on the galvanometer. By means of platinum wire and plate Hankel interposed the flame in the circuit of a Bunsen's element and obtained deflections of 34 and 294 divisions of the scale according as the current went from the large to the small surface or conversely. He showed that this deflection did not remain constant with a number of elements, but increases considerably with the electromotive force, and he pointed out the relation which this must have with the deportment of Gaugain's valve.

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* Ueber das Verhalten der Weingeistflamme in elektrischer Beziehung (*Abhandl. der math.-phys. Classe der K. Sächs. Ges.* 1859). Pogg. *Annalen*, vol. cviii. p. 146.

The connexion between the resistance at the kathode and the occurrence of the glow-light is at present of great interest, and led me to examine them, and more particularly in Bunsen's burner.

60. It can be shown by the flame in the first place how greatly the conductivity of gases increases with the temperature. If, for instance, the combustibles are fed with pure oxygen instead of with air, far greater current-intensities are obtained under the same conditions. Unfortunately, we have no electrodes which are suited for the study of these hottest flames. For platinum wire melts in so short a time that the needle cannot assume a steady position. The only good conductor which still retains the solid form, gas carbon, burns on the surface and becomes covered with ash, which exerts a disturbing influence.

In order to get at any rate a few numbers I supplied the coal-gas instead of oxygen with a mixture of three volumes of this gas and two volumes nitrogen, and have used the lamp which is in general use for glass-blowing. The platinum wires melt also in this to beads, though less rapidly when the diameter exceeds 0·5 millim. One Bunsen's element gave in a long-wire galvanometer a permanent deflection of 73°, while in the non-luminous Bunsen's flame it amounted to only 3°. From his experiments on dissociation Deville estimates the temperature of the oxyhydrogen flame, which in any case is higher than ours, at 2400° C., while the hottest parts of Bunsen's flame will be at 1500°. Hence for this difference of thermal conditions the increase of resistance is very considerable.

61. If the Bunsen's flame is interposed in the circuit of a voltaic element by means of two platinum wires, the same deflection of the galvanometer is observed however different be the distance between the electrodes if the position of the kathode is not changed. The needle recedes only when the positive wire has passed from the hot cone into the colder part. This experiment shows that the resistance of the flame is infinitely small compared with that in the neighbourhood of the kathode. We must take care, however, that the kathode is not displaced, for in that case very different deflections are obtained. The greatest deflection is obtained when the kathode is in the hottest part, which is known to be directly above the point of the inner cold cone, and in this way we can very easily learn something as to the temperature of the flame.

In the above flame also which is fed with air richer than usual in oxygen, the resistance at the negative pole preponderates so greatly over that of the other gaseous stratum that the alteration of distance has no influence on the strength of the current.

This fact seems at first sight to be in disaccord with the result which was given by the tubes described in § 3. The resistance of a greater length of the positive light disappeared in comparison with that of the glow-light only at pressures less than 1 millim., while at such pressures as exist in those flames the enfeeblement of the induction-current was preferably due to the positive light. We must, however, consider that the conditions in these two cases are different. The gaseous medium of the tubes must first be raised by the current to that high temperature at which it perceptibly conducts, and in this process it will develop a great resistance, which is entirely wanting in the body of the flame. In very rarefied gases the quantity of heat required for the rise of temperature of the small mass is insignificant, and hence the conditions in this case approach more nearly those afforded by the flame.

62. The resistance of the flame would probably be inversely proportional to the surface of the kathode, if the same temperature could be produced all over the latter, and if the relatively small mass of gaseous matter were not materially cooled by the introduction of such large well-conducting substances. Only with small changes of the negative surface is there an increase of conducting power approximately proportional with it. The influence of temperature may completely conceal that of surface in a Bunsen's flame. Thus, when a platinum wire was placed in the axis, and terminated in the hottest part of the apex of the blue flame, while a thin cylinder of the same metal of about 1 cm. diameter surrounded it, a greater deflection was obtained with the wire as the kathode than with the foil.

63. At the temperature of our flames in which the gases had so great an electrical resistance, other vapours have already a far greater conductivity. Of all vapours that of potassium conducts the best. After it comes sodium. The rest of the metals, in so far as they are volatile (the rare ones I have not examined), make very little alteration in the deflections in the gaseous state. It is unnecessary to introduce these elements into the flame in the free state; all their compounds which volatilize can be used.

In this experiment two platinum wires were symmetrically placed in the same horizontal section of the cone, and were connected with the voltaic cell and the galvanometer. A third platinum wire, the end of which was formed into a loop, contained the substance, and was placed lower in the flame, so that the vapours surrounded the other two uniformly.

The spectrum of the light which the salts develop teaches that the combinations of the alkalies are decomposed and the metals are partially present in the free state in the flame. In these researches I have found a fresh fact which I will mention. If the bead of a potassium salt, like the carbonate, in a loop of platinum wire is placed free in the axis of a porcelain tube which is heated to whiteness by a charcoal fire and air is passed through, the salt remains without alteration in the loop, and is therefore non-volatile at this temperature. But if hydrogen is passed instead of air, the bead disappears from the wire. This is only possible if it is reduced to the metallic state, which then volatilizes.

The deflections of the galvanometer which are found under these circumstances show how much greater is the conductivity of alkaline vapours compared with that of other gases at the same temperature. Two Bunsen's elements gave in a pure Bunsen's flame the deflection of $3\frac{1}{2}°$. When an oxygen salt of potassium was introduced, the needle oscillated violently about 90°. In order to make comparisons one part of the current was deflected from the galvanometer. The vapours of KHO, KFl, KNO_3, K_2CO_3 were now seen to be the best conductors. To these followed K_2SO_4, and KPO_3, as they are less volatile. KCl, KBr, and KI are decidedly worse conductors. As they volatilize more easily than oxygen salts, it appears as if their reduction by the constituents of the flame gases is less easy.

The oxygen compounds of the sodium salts also conduct less easily than the haloids. All deflections are not inconsiderably smaller than with the corresponding potassium compounds. For electrical flame-experiments the platinum wires must be strongly ignited, and the chloride of sodium adhering to them be volatilized before constant results can be expected. The higher conductivity of the oxyhydrogen flame is also considerably increased by potassium and sodium salts.

64. The low resistance of potassium vapour may be very well utilized to show in a striking manner the great enfeeblement which the voltaic current experiences at the negative pole in our flames, and is an experiment which by its simplicity is adapted for the Lecture Room. If a platinum wire, with a bead of potassium carbonate, is placed in the upper layer of a Bunsen's flame, and is thus surrounded with potassium vapour, while there is a blank wire in the lower layers, the deflection of the needle is very different according to the direction of the current which passes through the flame. When the bead is negative the needle is driven against the stops; if it is positive the deflection for the same element only amounts to a few degrees.

If the loop with the bead serves as negative pole, the resistance of the unaltered column of flame is again preponderant in comparison with that of the vicinity of the kathode. For with a decrease in the distance between the electrodes the deflection of the needle increases considerably.

In order to prevent any general increase in the conductivity of the flame, by the salts passing into the air of the chamber and then returning, I enclose the lower half of a Bunsen's flame in a glass vessel to which the air is led from outside by a wide tube. The flame burns underneath a tube which opens into the narrow chimney of a stove, and carries away the finely divided salts with the ascending current of air.

The above experiment gives the same result with the flame which is richer in oxygen, and shows that with this better conductor the enfeeblement of the current takes place mainly at the kathode.

65. On the other hand, I was not successful in proving positive unipolarity for the vapour of potassium itself when present in the Bunsen's flame. In this case varying deflections are obtained for different distances between the electrodes, and when a wire and foil are used almost the same intensities are obtained whatever the direction of the current.

If this result were firmly established it would be of great importance. But it needs a sharper test than the flames allow of. As yet I have not been able to devise a method by which the entire flame could be simultaneously charged with potassium vapour. To this difficulty a second is added. The bead of the volatilizing salt is the seat of an electromotive force, and produces a current which proceeds in the flame towards the clear wire. When I endeavoured to compensate that force by known electromotive forces according to Poggendorff's method a great variability was met with. The force may be greater than that of a Daniell's element when the bead is large, and it decreases with it. It comes into play between two wires when they are in different parts of the flame if they contain different quantities of metal vapour. As differences of temperature of the electrodes also produce currents, two platinum wires in the flame which is made a conductor always give a deflection of the galvanometer, and cannot be kept homogeneous. The investigation requires a space filled exclusively and uniformly with potassium vapour of constant temperature.

I was not able to confirm Erman's observation in reference to the negative unipolarity of phosphorus flame, as to which, however, he was not fully convinced. In my investigation of the isomerism of phosphorus * I observed that its vapours under low pressure show the same luminous phenomena under the action of the induction-current as other gases, and decidedly liberate glow-light at the negative electrode.

Without complicated arrangements the flame of phosphorus is difficult to handle, but gave with the galvanometer no indications of such an abnormal deportment.

66. An important fact, deserving our close attention, is that mentioned above, discovered by E. Becquerel and Hankel, of the dependence of the resistance at the kathode on the magnitude of the electromotive force of the element. I have frequently observed it in Bunsen's flame with very different numbers of elements. Thus, for instance, using one element I observed a deflection of 4°, and with 24 elements 11½° in the galvanometer.

The hotter flame shows the same effects. The deflection of 3° which one element produces (only part of the current went through the galvanometer) was only 8° when there were thirty.

It can be very well shown by means of potassium vapour that only the neighbourhood of the kathode effects this result, and that in both flames the resistance of the gas is approximately constant when the number of elements is increased. For if this experiment is repeated when the negative wire has a loop with potassium carbonate, and is in the upper part of the flame, while the clear positive wire is in the lower part, currents are obtained which are almost proportional to the number of elements.

It is probable that the neighbourhood of the kathode is not only the seat of a resistance, but also develops counter electromotive forces which contribute to the enfeeblement of the current.

67. The observations recorded in these paragraphs I consider as only preliminary studies and reconnaissances, which are necessary since the field is so unknown; and the second method, the only one which allows of accurate measurements, presents great difficulties in its execution.

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* Pogg. *Ann.* vol. cxxvi. p. 222.

Hitherto only one research has appeared in which the conductivity of ignited homogeneous gases for voltaic currents is investigated. It was published by E. Becquerel in 1853*. I soon saw when I began to work at this subject, last winter, that the shape of Becquerel's gas-receiver is not advantageous, and must be replaced by another if concordant results are to be obtained. Unfortunately vessels of this kind, which must be of porcelain, are not met with in commerce, and in the very unfavourable circumstances in which I had to make my experimental investigations, I could not procure any. When I succeed in doing so I think of resuming my investigation and of using the results for a further communication.

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* *Ann. de Chim. et de Phys.* series iii. vol. xxxix. p. 371.

ON THE CONDUCTION

OF

ELECTRICITY IN GASES.

BY

PROFESSOR W. HITTORF.

PART II.

Ueber die Elektricitätsleitung der Gase. Zweite Mittheilung.
Poggendorff's *Annalen, Jubelband*, 1874, pp. 430–445.

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68. When, after a long interval, I returned to the investigation of the conductivity of gases, I felt more strongly than before the necessity of being able to work with the current of the voltaic circuit, as well as with that of the induction-coil and of the electrical machine, for it has been most minutely investigated in every direction. The reason why the phenomena of lightning, the best known of all electrical phenomena, are still so little understood, may mainly be due to the fact that the cells in ordinary use, with their small tensions, cannot produce the phenomenon in question. The experiments which physicists of the last century made with the electrical machine were also insufficient to explain the accurate deportment of metallic and electrolytic conductors, as we now know them. This insight was only attained after Volta had enriched science with his battery.

Gassiot* has the merit of having been the first to show experimentally, that the enigmatical luminous phenomena, which the induction-currents of Ruhmkorff's coil produce in a rarefied space, can also be produced by the galvanic circuit, provided there are a sufficient number of elements to produce the requisite tension. Besides a battery of 3520 cells, consisting of zinc, copper, and rain-water, he used a Grove's battery of 400 elements. By means of the latter two different kinds of discharge were produced in tubes with rarefied gases. Immediately after closing, the stratified light formed at the anode and the glow-light at the kathode, just as with induction-currents. A dark space separated the two, and the negative wire was most strongly heated. This discharge, which for the sake of brevity we will call the *glow-discharge*, passed spontaneously after a short time into that which essentially coincides with Davy's luminous arc, and shall for the future be designated as the *arc-discharge*. In this case those differences of the light at the electrodes, as well as the dark space, have disappeared. A coherent mass of light joins the poles, of which the positive is the strongly-heated wire. While the intensity of the current remains feeble in that first discharge, it increases considerably with the commencement of the arc-discharge.

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* Pogg. *Ann.* vol. cxix. p. 131.

69. The gaseous medium presents here, during the first discharge, just such large resistances as are met with in using the induction-current—resistances in comparison with which those of the elements themselves are insignificant. It must thus be possible also to produce the glow-discharge if the individual elements have small dimensions. Only a few physicists have at their command 400 Grove's elements of the usual type. But even where they are available, the putting them together and taking them asunder, will be found to be so tedious and require so much time that they can but seldom be used.

The matter is otherwise if the manipulation of such a battery is not more troublesome than that of a single cell. This may be obtained by taking small dimensions, and fixing the metals so that they can all be immersed in or removed from the liquid.

In the battery which I constructed in this manner the individual elements consisted of amalgamated zinc, carbon, and the mixture recently given by Bunsen—bichromate of potassium and sulphuric acid. This combination recommends itself by its great electromotive force and the simplicity of its arrangement. It has the disadvantage that the electromotive force diminishes as the reduction of the chromic acid progresses, and that the zinc is attacked by the liquid even when the circuit is open. The combinations in which, as in Daniell's element, there are primary decompositions only, are far more constant. I should have preferred them, if, owing to their having two liquids, it had not been necessary to sacrifice simplicity and facility of manipulation.

Zinc wires, such as can be obtained commercially of all diameters, are best suited for preparing small elements. I use them of the length 155 mm., and the diameter 6 mm. The carbons have the same length, and are sawn from large blocks of gas-carbon, in parallelopipedal pieces 7 mm. square. Each of them is filed round in the part which is not to dip in the liquid, and, like the zinc rods, is cemented with sealing-wax in a glass tube which only leaves the top free. A zinc and a carbon are put in a cork. Three boards with holes are used for keeping the elements in place ; the holes have the diameter of the cork, which is also that of the vessels for the liquids. The glasses are cylindrical, 120 mm. in height and 30 to 35 mm. in diameter ; they stand upright in a frame constructed of two of the boards. The third board, in the holes in which the corks with zinc and carbon are fastened, can be raised and lowered by a simple arrangement, and fixed at any height.

In order to ensure that the elements are in easy and perfect contact with each other, the pieces of carbon were previously coppered galvanoplastically and then tinned. Hence after being fixed in their places they could be easily connected by copper wire with the next zinc wire. As the number of elements required varied, and in order to avoid as much as possible unnecessary consumption of zinc and solution, it was arranged that not the entire number, but only what was requisite in each case, should be brought in contact with the liquid. The movable board consisted of five portions, each of which could be lowered separately. The galvanic battery thus arranged contained 400 elements, which formed 20 rows and 5 divisions of 20, 40, 40, 100, and 200 elements. Its length was 115 cm., breadth 82 cm., and it could therefore be very easily manipulated. I am constructing a second battery of 400 elements which are fixed to one board, so that I shall afterwards be able to work with 800 elements.

Although each individual zinc rod is in a glass tube, the insulation is not found to be quite perfect. In order to avoid possible disturbances arising from leakage of electricity to earth, the wooden frame rests on four glass cylinders, 11 cm. in height and 8 cm. thick, coated with sealing-wax.

This battery can easily be converted into the chloride of silver element recommended a few years ago, if the zinc rods are made shorter than the carbon rods, and if chloride of silver is placed so high on the bottom of the vessel that only the latter are in contact with it.

The 400 elements quite come up to the expectations which I had formed of them, and in sufficiently rarefied gases give the luminous phenomena of Ruhmkorff's coil. They have even exceeded my expectations, as under certain conditions they also produce the arc-discharge.

70. The longer I busy myself with the discharge of electricity through gases, the more I am convinced that the enigmas which here present themselves will be solved when the electrical relations of matter in the third state of aggregation at high temperatures have been investigated. At a red heat all gases, as we shall see, lose the insulation which they possess at a low temperature, even for feeble tensions, and may be called conductors with just the same right as metals and electrolytes, even if the process itself is essentially different and its laws are completely unknown. Their conductivity increases with the temperature of ignition in a rapid ratio, such as we do not find with solids and liquids*. So long as these important facts are not more closely investigated, the basis for the subsequent construction of a theory will be wanting.

The experimental difficulties met with in the direct investigation of the above problem compel us to try any means by which we can explain that process. Such high temperatures can be most conveniently obtained in those gases which combine with oxygen with considerable production of heat, and therefore produce flame in burning. The numerous flames which Chemistry furnishes, are therefore very suitable for our purpose.

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* In the second edition even of his valuable Handbook (*Die Lehre von Galvanismus und Electromagnetismus*, vol. i. p. 339) Wiedemann wrongly doubts the accuracy of the results obtained by E. Becquerel that ordinary gases conduct at a red heat. I have repeated the experiment in question in a tube of suitable shape, and will give the results in the sequel.

In connexion with the last paragraphs of my first communication I will first of all specify the observations which I have made on the electrical deportment of flames.

71. The remarkable phenomenon of positive unipolarity, which Erman discovered at the beginning of the present century, I have met with in all the flames which I have examined. The discoverer failed to obtain it with the flame of sulphur; and with that of phosphorus he thought he had found the opposite, that is a negative unipolarity. I produced both flames by heating each substance to boiling in an iron crucible over a well-insulated lamp; the crucible had a tightly-fitting lid, and the column of vapour which issued could be burnt under a good draught. The interior of the flame thus formed is at a low temperature; only the narrow sheath, where combination with the oxygen of the air takes place, is hot. If under these conditions the pole-wires of the voltaic battery, which were connected with two equal ordinary gold-leaf electroscopes, projected into the flame, the divergence of the gold leaves was scarcely altered by holding in it a third wire connected to the gas-pipes. (Iron wires must be used with phosphorus, for platinum is attacked by it.) The result was different when a glass tube was held over the aperture of the crucible, and air from a gasholder was forced into the column of vapour. As the combustion now produced a high temperature in all parts of the flame, the third wire at once made the positively electrical gold leaves collapse, and caused the negative ones to diverge twice as widely, just as with the flame of coal-gas.

72. The cause of the positive unipolarity of flame must be sought in a difficulty of conduction near the negative pole, like a resistance of transition. The opinion expressed by Ohm that an opposing tension may wholly or partially produce the enfeeblement is unfounded. I convinced myself of this by rapidly passing the current in alternate directions through the flame, and observing the strength of this current in a sensitive Meyerstein-Meissner's galvanometer with 18,000 turns, which had a resistance of 3630 Siemens' units. These rapid alternations were produced by a special arrangement

which I shall describe in its place. The deflection was not greater than when the current was passed through the flame for the same length of time in constant direction.

73. The ratio of the resistance at the kathode to that in the rest of the path of the current, can be approximately determined by surrounding the negative pole with potassium or sodium vapour, the good conductivity of which I called attention to in a previous communication. The flame of an insulated Bunsen's burner was surrounded by a chimney as far as the inner blue cone extended, and was placed under a draught; in this two loops of platinum wires 0·2 mm. in diameter were placed vertically above each other, at a distance of 45 mm. The lower loop was just above the point of the inner blue cone, the upper one in the higher parts of the luminous flame. The current of 20 freshly filled elements was passed through the flame by means of these loops—in one case when they were empty, and in the other when there was a bead of potassium carbonate in the upper one. The above-mentioned galvanometer, which was not astatisized, took only a portion of the current—that which its interposed wire of 500 mercury units shunted. This arrangement was made in order that various deflections could be read off on the scale.

The deflection amounted to only 2·2 mm. when both loops were empty, in whatever direction the current traversed the flame. No alteration was perceived when there was a bead of CO_3K_2 in the upper loop, and it acted as anode. The deflection varied between 280 and 320 mm. when the evaporating bead surrounded the negative pole. The resistances of the galvanic elements, and of all the wires, may be neglected in comparison with that of the body of the flame. I have satisfied myself that the latter is so considerable, that in the circuit containing the flame, the deflection of the galvanometer is not appreciably altered by the insertion of 10,000 mercury units. We must, therefore, conclude from these numbers that the resistance at the kathode is $\frac{300}{2{\cdot}2}-1$ $=135$ times the resistance of the rest of the flame. Almost the same ratio was obtained when the number of elements was 40 and 300. The ratio is, however, less when the number of elements is small. Thus with 2 it was 45. This difference is occasioned by an error in the method which the more affects the result, the smaller is the electromotive force used. The evaporating bead of CO_3K_2 produces, as we shall see, a current which, in the flame, is directed towards the empty loop, and the electromotive force of which is no inconsiderable proportion of that of one of our galvanic elements.

74. In order to establish whether there is a similar, if smaller, resistance to the flame-gases in the neighbourhood of the positive pole, two lamps were employed, such as are used by glass-blowers. They consist, as is well known, of two concentric tubes, the inner one bringing air, and the outer annular one coal-gas. Owing to the velocity with which the gases issue, the flame retains its shape at whatever angle it be placed. Both lamps were insulated, and so arranged that the flames touched at the base, and diverged upwards at an angle of about 60°. In this way a flame was obtained with two points, in which by means of platinum loops, and the beads of CO_3K_2, good conducting potassium vapour could be introduced without its reaching the other parts. The whole was placed under the funnel-shaped enlargement of the draught tube, which conveyed away the products of combustion along with the particles of salt.

Now, when in one case only the negative bead, and in the other both loops contained CO_3K_2, it was seen that the deflections of the galvanometer were practically equal. The resistance at the anode is therefore so small that it does not come into play in this method.

75. If in the experiment (73) the lower loop is provided with CO_3K_2 instead of the upper, and thus the entire path is made of this material, it will be seen how greatly the conductivity of potassium vapour exceeds that of the flame-gases. In order that the deflections could be read on the scale, only that portion was passed through the galvanometer which branched from a shunt circuit of 2 mercury units, and the number of the elements used was reduced to 5.

When there was a bead in the upper loop, and none in the lower one, the deflection was 1 mm. When there was a bead in the lower one, and therefore the entire space between the two loops was filled with potassium vapour, and the distance of the loops was 45 mm. as above, the deflection was 180 mm. and rose even to 215 mm.

Potassium vapour conducts so well at the temperature of Bunsen's flame that there will be no difficulty in accurately determining its resistance in terms of the other units as soon as a method is found of obtaining it constant. The evaporation of a bead cannot so be considered. In a quantitative experiment which I made, two pieces of the same platinum wire were placed at a distance of 3 mm. in the same horizontal section of the flame, and were so completely surrounded with potassium vapour from a bead beneath that no current passed between them in the galvanometer. When I determined the resistance, by means of Wheatstone's bridge, it was found to be greatly dependent on the dimensions of the bead. The larger the latter the greater was the resistance, and it diminished with the disappearance of the salt. It was least at the moment the last particles evaporated, and had usually sunk below half its first value. Evaporation and dissociation of the salt undoubtedly considerably cool the gases, and the conductivity must be materially influenced by this difference in temperature.

Although potassium vapour seems a good conductor in comparison with the gases of flame, it is a much worse one than solid and liquid metals. Under the above circumstances resistances of 1500 to 3000 Siemens' units were found.

76. At the temperature of Bunsen's flame potassium vapour also presents a greater resistance to the flame at the kathode, and is hence in a certain sense positively unipolar. This is seen as follows :—equal parallel platinum wires, which are at a distance apart of 3 to 4 mm., are in the same horizontal section of the flame and are uniformly coated with potassium vapour by a bead held beneath ; a current is thus transmitted for which the number of elements is gradually increased. The thinnest wires which I could procure were obtained from the sponge of a Doebereiner's lamp. Using these, thirty elements were sufficient to make the negative wire brightly incandescent. With 40 elements it melted, while the positive was unchanged, and showed no greater incandescence on ignition. With thicker wires ($\frac{1}{5}$ mm.), 60 elements were needed to fuse the negative wire slowly to a bead. 80 elements were

necessary to obtain this action with wires of $\frac{1}{3}$ mm. At this diameter the positive wire began to melt slowly when 140 elements were used, and the negative rapidly. With 200 elements and upwards no difference could be perceived in the rapidity with which they melted ; as soon as the bead of salt was placed below, both electrodes ran into beads to the edge of the flame. The arc-discharge is now complete. Platinum wires of the thickness of 3 to 4 mm. melted at the ends when they served as poles of the circuit in potassium vapour.

Thin cylinders of good conducting gas-carbon were found unsuitable for showing the transition of one discharge into the other, perhaps because the eye does not recognize the difference in the strength of the incandescence. The discharge takes place with a smaller number of elements when they are separated from each other by the above distance. About 80 were necessary for this. A much smaller number is of course necessary if the electrodes are first brought in contact in potassium vapour, and are then drawn apart. With 300 elements the discharge in potassium vapour takes place with a separation of the electrodes of 4 to 5 cm. During this process by far the greater part of the current is conducted by the smaller mass of potassium vapour, which becomes strongly heated, and is distinguished by greater development of light. The points of both carbons which they bound are strongly incandescent. If the ends are opposite each other in the same horizontal section of the flame, the current forms an arc as in air. The incandescent spot continually changes its place on the kathode, while it retains its place on the apex of the anode.

77. The battery described has a very small striking distance in air of ordinary density and temperature. In order to obtain here the spark of 400 elements, the poles had to be brought almost in contact. As my spark-micrometer was not constructed solidly enough for measuring small distances, I used a micrometer the steel screw of which had windings 1 mm. in height, whose disk was divided into 360°, and which stood on a smooth glass plate. Below the slightly rounded end of the screw, which served as one electrode, there was a steel plate for the other. The position of the screw at which it touched the plate could be determined to

within $\frac{1}{1000}$ mm. by using Poggendorff's excellent method. This apparatus was first introduced into a circuit which consisted of only a single element and an ordinary galvanometer. When the screw was turned a deflection of the galvanometer showed when the point and plate touched. When the corresponding division of the disk had in this way been found, the separation was effected and both parts connected with the poles of the battery. By means of three mercury cups this operation could be readily effected in the well-known way. By slowly turning the screw backwards the division which faced the mark when the spark passed could be observed, and the length of the latter be thus determined.

With 400 elements the point of the screw had to be brought to within $\frac{21\cdot3}{360}$ to $\frac{20\cdot2}{360}$ mm., or about $\frac{1}{18}$ mm. from the plate, to obtain the spark. There was no appreciable difference whether the former was positive or negative. 300 elements showed a striking distance of $\frac{12\cdot6}{360}$ to $\frac{15\cdot5}{360}$ mm. With 200 elements the individual determinations differ greatly, but with 20 elements the striking distance is at $\frac{1}{360}$ mm. The cause of these differences is to be sought in the changes which each spark makes in the surface of the electrodes. On the steel plate they can be made innocuous, as a fresh plate can be taken for each determination. This, however, was impossible with the point of the screw, and a simple rubbing had to suffice.

The first spark seems always to be a glow-discharge. In most cases it changes so rapidly into the arc-discharge that its nature cannot be determined. This, however, is very easy if the electrodes are platinum wires 3 to 4 mm. in thickness, and are so near that the luminous discharge takes place between the end of the kathode and a place on the anode which is distant from the end. The latter touches the former in only a small surface, and spreads out, forming a disk of glow-light which covers the section of the positive wire. If this light only lasts a short time it makes the end of the kathode glow and melt, while the anode does not become much heated.

If the electrodes are first brought in contact, and are then slowly separated, the arc-discharge is obtained in air, as is well known. The arc shows for the same number of elements great differences in length and duration, according to the nature of the conductors which serve as poles. These phenomena have been investigated by several physicists with batteries having a smaller number of elements but of greater dimensions. Such cells are also more suited for this purpose than our battery. For as the resistance of the Davy's arc is comparatively small, and the strength of the current is therefore great; the chromic acid is reduced at the surface of the small pieces of carbon at a quicker rate than that at which fresh acid is supplied. Accordingly, as the current continues the electromotive force sinks considerably, and the arc is soon extinguished. Hence also by separating the two conductors the arc will be so much the shorter the more frequently the experiment has been made in succession. If then the battery is lifted out of the liquid, and is again immersed, the longer arc is reproduced.

If the method first applied by Herschel is used, and the discharge of the battery is passed through the spark of the Leyden jar, when the electrodes are at a great distance, the Davy's arc is also at once obtained.

78. A new and instructive method of obtaining the discharge of the battery through longer layers of air results from our earlier experiments. They have shown that in pure gases of flame there is a very considerable resistance at the kathode, in comparison with which that of the rest of the circuit vanishes. We find here not much greater striking distance than in ordinary air; by shortening the length of the path no great change is made in the total resistance. But as soon as we place the kathode in the apex of the flame and surround it with potassium vapour, thereby eliminating that resistance, then on approaching the anode of 100 or more elements the feeble current which we had previously investigated passes into the strong arc-discharge even at considerable distances. With 400 elements the distance may exceed 10 mm. When the arc-discharge begins, the positive wire at once melts, forming a bead.

Just the same result is obtained if we put the anode in the outer cold air which surrounds the flame, while the kathode remains in the sodium vapour. The discharge of the 400 elements ensues when the distance of the point of the positive wire is 10 mm. from the potassium vapour. With 300 elements the greatest distance is 7 mm., with 200, 5 mm., and with 100 elements about 3 mm.

In the last three cases the formation of the glow-discharge is very beautifully seen. Only on the extreme edge of the anode is there a very small brush of glow-light, which is separated from the flame by a dark space. Air accordingly conducts at temperatures at which it does not visibly glow. If the distance is smaller a feeble yellowish light forms in the dark space in the prolongation of the brush, and now the strong arc-discharge occurs, which melts the wire. If carbon is used instead of platinum wires the course is the same. Hence at the greatest distance the carbon point nearest the flame appears with the brush of positive light. With 400 freshly filled elements, the glow-discharge is more difficult to perceive, for the distances at which it first forms almost coincide with those at which it passes into the strong arc-discharge.

If the poles are interchanged in our experiment, the anode being put in potassium vapour and the kathode outside the flame, the latter must be put in the sheath of potassium vapour in order to close the current. The phenomena mentioned in previous articles occur then.

It is thus proved that for ordinary air also, the striking distance, as determined in the previous articles, is due essentially to the great resistance at the kathode, and disappears with it.

79. As the heat of incandescence increases, the resistance at the kathode rapidly diminishes. This is seen already in Bunsen's flame. The hottest part is then in the point of the inner blue cone. If one wire is placed there while the second is placed in any other part in the flame, on passing the current through, twice as great a deflection is obtained with the former as kathode than with it as anode. With 20 elements, for instance, I obtained in the first case the deflection 42 mm., in the second case only 16 mm., when the entire current passed through the Meyerstein galvanometer which formed part of the circuit.

In flames fed with pure oxygen, gaseous media of much higher temperatures are afforded. It will be interesting to pursue our resistances in a similar manner. We can procure still higher temperatures than even the oxyhydrogen flame by passing powerful electrical currents through the most infusible of all bodies, well-conducting gas-carbon. All these means are available for the investigation of the discharge in rarefied gases. By using them we shall be able, with surprisingly low tensions of a few elements, to produce the glow-discharge in rarefied gases.

Münster, October 10, 1873.

ON THE CONDUCTION

OF

ELECTRICITY IN GASES.

BY

PROFESSOR W. HITTORF.

PART III.

Ueber die Elektricitätsleitung der Gase. Dritte Mittheilung.
Wiedemann's *Annalen,* vol. vii. 1879, pp. 553–617.

[PLATE III.]

IN the *Jubelband* of Poggendorff's *Annalen*[*] I have described a galvanic battery of 400 Bunsen cells of small dimensions, each of which consists of zinc, carbon, and chromic-acid solution, and arranged as an immersion battery. This battery had just been completed when I was asked to make a contribution for the celebration of the Jubilee; the contents of that short communication describe some experiments I had made with it. Since then I have devoted my scanty leisure to investigating the electrical conductivity of gases. In order to demonstrate all the known phenomena of the spark-discharge by the help of voltaic electricity, although only on a small scale, I have gradually increased the number of cells, and for the last year and a half have been in possession of an immersion battery of 1600 cells. The 1200 cells which were added later possess an essential improvement. Glass cylinders 300 mm. high were used to contain the liquid instead of vessels 120 mm. high, according to Bunsen's direction. The fitting up of the first 800 cells was a difficult task, as the small carbon parallolepipeda had to be sawn from larger pieces of gas-carbon, and, as already mentioned, turned cylindrically at one

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[*] *Vide anteà,* p. 167.

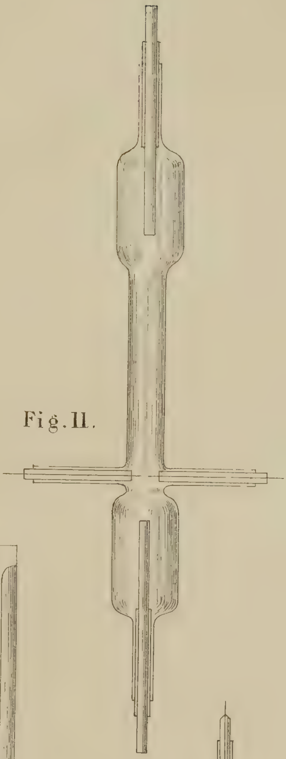


Fig. 11.

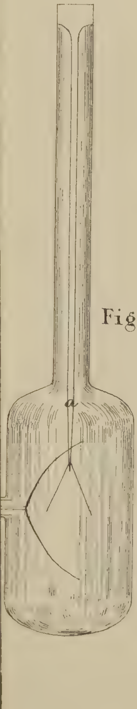


Fig. 10.

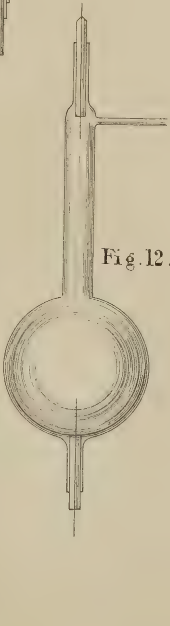
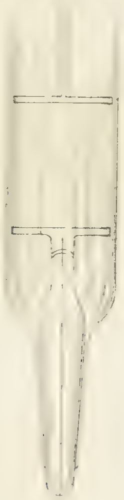


Fig. 12.

Fig. 1.



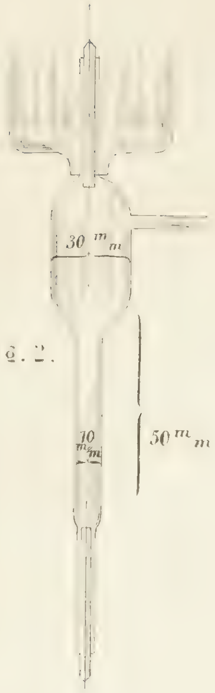
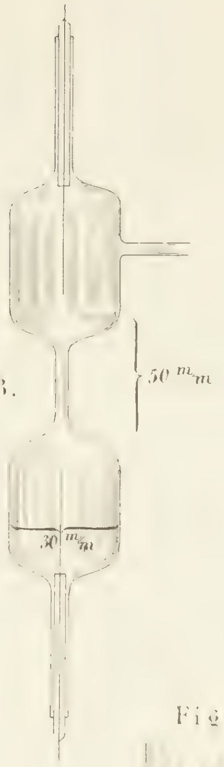


Fig. 2.

Fig. 3.



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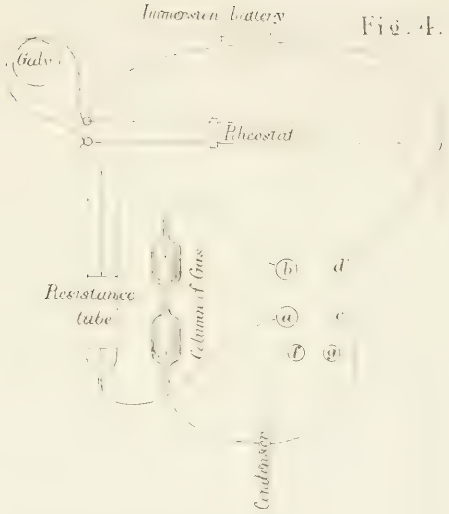


Fig. 11.

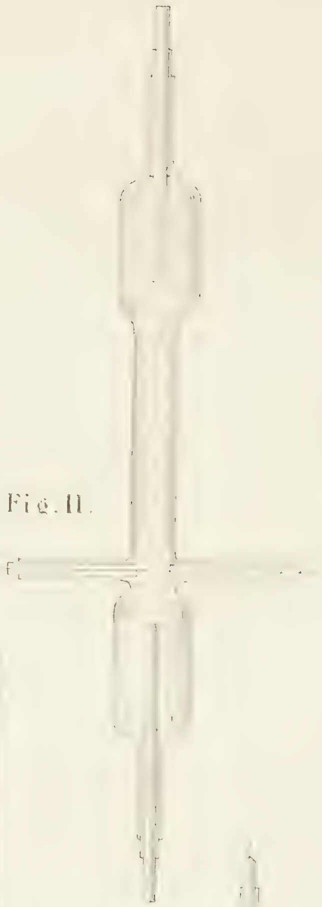


Fig. 6.

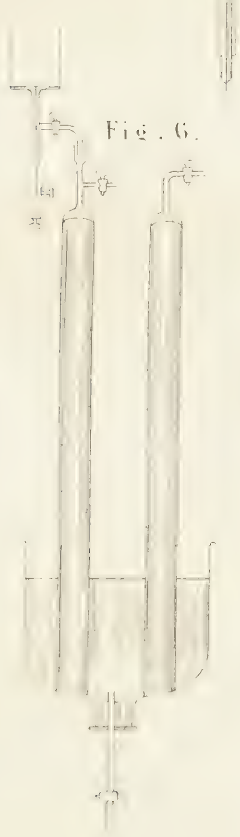


Fig. 5.

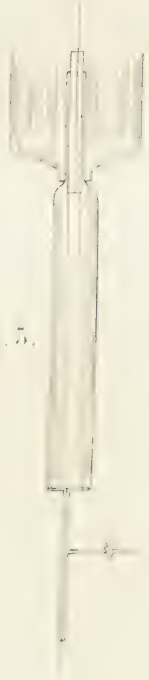


Fig. 7

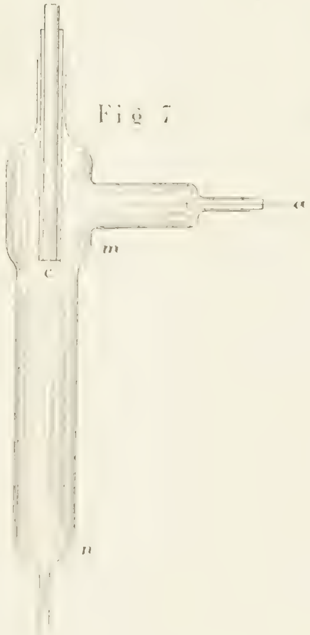


Fig. 8.

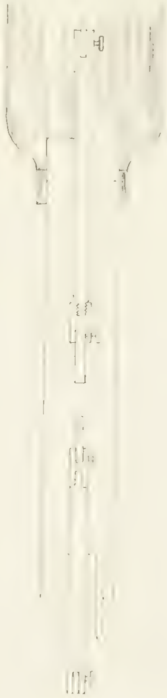


Fig. 9.

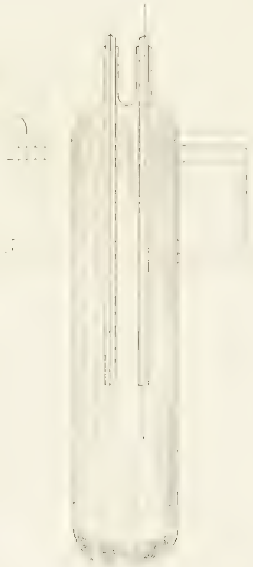


Fig. 10.

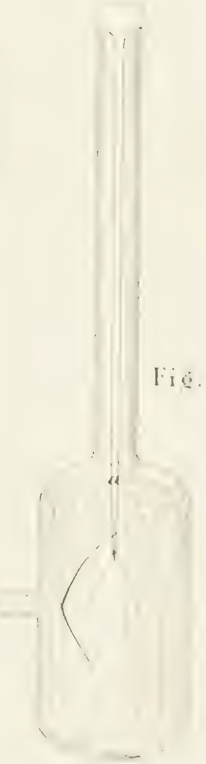
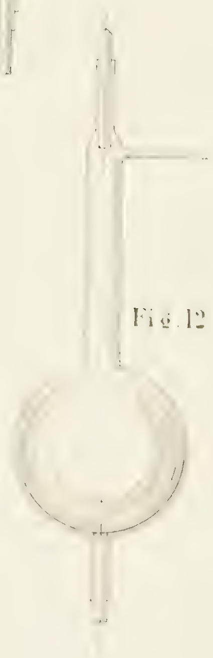


Fig. 12.



Mintern Bros. lith

end. In 1876, at the International Exhibition of scientific apparatus in London, I heard of the carbon cylinders made by Carré, of Paris, for electric lighting, and used them for the other 800 cells. Since carbon and zinc cylinders are now to be obtained commercially, it has become an easy task to fit up such batteries of a large number of cells, which are indispensable for the investigation of the electrical behaviour of gases, and I do not doubt but that they will soon be introduced into laboratories. In order to make the battery as convenient to use as possible I have attached each 200 elements to a board, as already described. They can be dipped into the liquid to any desired depth.

§1. The idea I had in view in fitting up this battery is manifest. With the help of this most efficient of all known sources of electricity, I hoped to produce the so-called glow-discharge in gases continuously, and thus obtain the great advantages for the investigation, which a continuous current offers, in contradistinction to a discontinuous one.

Gassiot, as is well known, was the first who obtained the phenomena which the electrical machine and the induction apparatus produce in rarefied gases, in an exactly similar manner by means of a battery of 3620 elements, which consisted of zinc, copper, and rain-water, and later by means of a battery of 400 Grove's cells. He found with the help of the rotating-mirror that both batteries certainly gave discontinuous discharges in his tubes, since images succeeding each other very quickly, and separated by dark spaces, appeared in the mirror*. On the other hand, the light of the Davy arc appeared in the rotating-mirror as a continuous band. This latter is also corroborated by other physicists. From these results Gassiot concluded that the stratified discharge in gases is never a continuous one, a conclusion which was accepted by many physicists as correct. At all events, Stokes †, De La Rive ‡, and G. Wiedemann § assent expressly to this view. When I expressed a doubt as to its correctness in an assembly of distinguished German physicists during the

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* Pogg. *Ann.* cxix. p. 131, 1863. † Ibid. cxxiii. p. 489, 1864.

‡ Ibid. cxxxi. p. 457, 1867.

§ Ibid. cxlv. p. 235, 1872, and clviii. p. 35, 1876.

International Exhibition in the autumn of 1876, I found that this view was held by myself alone.

The following consideration soon led me to look at the results of Gassiot in another light, and to recognize a concealed fallacy in his conclusion. When the 400 elements were connected with the electrodes of an extremely rarefied gas, Gassiot obtained first of all the glow-discharge with the stratified positive light, dark space, glow-light, and strong heating of the kathode. This soon changed, apparently spontaneously (the cause will be alluded to later), into the arc-discharge, in which the negative glow-light was wanting and a continuous mass of light connected the electrodes. This possesses, as Gassiot also noticed, an incomparably greater strength of current. As it was, however, continuous and if Grove's battery can furnish the large amount of electricity necessary, it was not apparent why it should not be sufficient for the much smaller requirements of the glow-discharge.

It can readily be understood that the cells of zinc, copper, and rain-water always cause a discontinuous glow-discharge, and this is to be explained by the small coefficient of conductivity of the water. Davy's arc-light cannot, however, be obtained with it. The current, however great the number of cells, can never, according to Ohm's law, attain the intensity of a single cell which is closed in itself without external resistance.

The researches I formerly carried out as to the behaviour of the negative glow-light in very rarefied gases with the use of an induction-current, and published in the first communication, caused me to interpret the result which Gassiot's 400 Grove cells gave in a totally different way. I have alluded there to the extraordinary resistance which appears in the neighbourhood of the kathode, and increases so rapidly on continued rarefaction of the gas below a tension of 2 mm. This is mainly due to the fact that when the electrodes are at a very small distance apart even large tensions no longer discharge themselves in tubes, in which the air has been rarefied as much as possible by means of the mercury pump. Gassiot studied the brush-discharge with 400 Grove cells in his vacuum tubes, in which carbonic acid was removed by caustic potash, and in which there was, therefore, a great rarefaction. Metallic spheres of ½-inch diameter, and thus of relatively small surface, served as electrodes. Here were accordingly present exactly the conditions which I have pointed out in my first communication as rendering the discharge very difficult. According to Ohm's law, a given resistance has the same effect on the current at whatever point of the closed circuit it may be. It is quite immaterial whether it be in the generating-cells or at any point in the external closed circuit, or, as here, in one part of the gas itself. On these grounds I expected to obtain the brush-discharge continuously in all cases in which such great resistances are avoided, and in this supposition I have not been mistaken. Within wide limits my immersion-battery gives a continuous brush-discharge in rarefied gases ; it gives a discontinuous one when sufficiently large resistances are introduced into the outer circuit, or if they are present in one part of the gas itself, as is the case in Gassiot's vacuum-tubes.

§2. In order to give an experimental proof for this conclusion, I must first of all describe the method and the apparatus which I used.

The action and behaviour of his battery has been so exactly described by Bunsen, in recent times *, that any further particulars are superfluous. Bunsen finds that the electromotive force of his battery, when freshly charged and with larger resistances introduced, is somewhat greater than that of a Grove's cell. My small cells, in which the carbon rods are 8 mm. in diameter, when freshly filled, and immersed to a depth of 8 cm., have a resistance varying between 1·25 and 1·75 Siemens units, according to the distance between the zinc and the carbon. This resistance naturally increases with use in proportion as the well-conducting free acids disappear. After very long use I have even found it to be over 5 Siemens units. The total resistance of a battery of a given number of cells can in this way be easily computed. If the zinc and carbon rods are not immersed to the depth mentioned above, the resistance is of course increased in proportion. The resistance of the immersion-battery is very small in comparison with the resistances which are necessary for the investigation of the glow-discharge, and can in many cases be entirely neglected. It is only necessary to be certain

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* Pogg. *Ann.* clv. p. 230, 1875.

that the surface of the zinc is clean, and not coated with a layer of salt, since this, as is well known, causes a great resistance. My battery is so arranged that the wooden frame, with the part to which the carbons and zincs are attached, can be lifted from the glass jars. The zinc wires can thus be easily dipped into a trough containing dilute acid and be freed from a bad conducting surface-layer.

However great the number of cells, the strength of the current given by a battery in our experiments can never exceed that which a single cell yields when closed without any external resistance, and forms in most cases only a very small fraction of this maximum. Since, according to Weber's system of measurement, the electromotive force of a Bunsen cell amounts to about 194×10^9 units and 1 Siemens unit $= 9717 \times 10^6$ units, it follows that the maximum current which 1 cell produces in a circuit of 1·5 Siemens units' resistance must reduce in a minute $6{\cdot}779 \times \frac{194 \times 10^9}{1{\cdot}5 \times 9717 \times 10^6} = 90{\cdot}2$ mg. of silver *. In one experiment which I made the deviation caused by the maximum current of a freshly-filled cell corresponded to a deposition of 86·2 mg. of silver in a minute.

For measuring the strength of the current I generally used the Meyerstein-Meissner mirror-galvanometer †, already alluded to in my second communication. The thin wire makes 18,000 turns and has a resistance of 3620 Siemens units. It was shunted either from a Siemens resistance-coil or from two parallel platinum wires 1·1 mm. thick of a rheostat of ordinary construction, which, with a length of 2 × 100 cm. and at a temperature 12° C., have a resistance equal to 0·5873 Siemens units. Since the two wires can be varied in length by means of the slider, and the position of this can be read off at the graduations, the strength of current can be determined in the ordinary manner with the galvanometer, within wide limits. The magnet always retained its full directive force. The mirror was 4285 mm. from the scale of the observing-telescope. The above maximum current which reduced 86·2 mg. of silver caused a deflection of the magnet of 320 mm., when the wire of the galvanometer was shunted through the wires of the

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* *Vide* F. Kohlrausch, *Leitfaden der praktischen Physik.*

† *Vide* G. Wiedemann, *Lehre vom Galvanismus,* ii. p. 233, 1872.

rheostat 2 × 1 cm. in length. The statements made later as to the strength of current used are thus easily intelligible.

To be able to vary the strengths of the currents it was necessary to have resistances which amounted to many millions of Siemens units. Metal wires cannot well be used for this ; the larger Siemens resistance-coils especially cannot be used, since, as is well known, owing to the particular method of winding, sparks are formed at the ends and destroy them. For, in my first research *, I had experienced how variable and how dependent on the pressure is the resistance at the point of contact between such conductors and the metals ; a variability which in recent times has been turned to such beautiful practical uses. My choice was, therefore, directed solely to electrolytic liquids. Distilled water, which when kept in glass vessels may be considered as an extremely dilute saline solution, is generally used for the above purpose. I employed it only at the commencement of my research. It possesses the great disadvantage that its resistance continually decreases as particles of salt get into it from the glass and from the air. In my electrolytic researches I met with a liquid of very great resistance, most suitable for the above purpose, and which I have of late exclusively used. It is a solution of cadmium iodide in amyl alcohol. In order to be sure of obtaining the salt anhydrous I fuse it before dissolving ; the solution is prepared from 1 part by weight of salt to 10 parts of amyl alcohol. This solution is contained in cylindrical tubes, graduated in millimetres, between circular plates of amalgamated cadmium, which have nearly the same diameter as the tubes. The lower disk, which serves as the kathode, reaches as far as the zero of the divisions, and is attached as follows (Pl. III. fig. 1) :— An end-piece with a tubulure, which is narrowed conically towards the bottom, is fused on to the graduated glass tube. A glass tube had previously been ground into the tubulure containing a stout platinum wire fused into its axis, of which both ends projected. The latter is firmly connected to the cadmium plate by means of a projecting piece surrounding it, and by the addition of some mercury is converted into a solid, tightly fitting amalgam. In this way a cork is avoided, and there is no possibility of the part ground-in falling out owing

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* Pogg. *Ann.* lxxxiv. p. 8, 1851.

to the pressure of the liquid. The anode disk can be adjusted to any given distance up to 800 mm. from the kathode by means of a long cadmium wire, to which the necessary stability has been given by a glass tube surrounding it. The two electrodes must always be used in the position stated, in order, in the first place, that the great differences in concentration caused by the electrolysis at the surface * shall equalize themselves, and all sections of the liquid retain the same composition. Amyl alcohol has first of all the advantage over water of being less volatile, its boiling-point being 132° C. Moreover, it has no power of dissolving the constituents of the glass, so that the liquid remains unaltered. Unfortunately the cadmium which is liberated at the kathode does not combine with it, even when the surface is formed of mercury. Fine black particles become detached, which are doubtless an allotropic modification of the ordinary metal. The solution of cadmium iodide in ordinary alcohol behaves in a similar manner. The details I must reserve for a special communication. I used these resistance-tubes of four different diameters, viz. 4 mm. (I), 9·7 mm. (II), 17 mm. (III), 32 mm. (IV). For the sake of brevity they will be referred to by Roman figures. Since the temperature of these badly conducting liquids is appreciably raised by strong currents, and their resistance is thereby diminished, each tube is surrounded by a wide condensing-tube containing water, which can be renewed when necessary. The resistances of these columns of liquid were compared with a Siemens coil by means of the Wheatstone bridge. At a temperature 14°·6 C. 27·5 mm. of the widest tube (IV) had a resistance of 10,000 Siemens units. Resistances, when given below in terms of the lengths of the columns of liquid in question, can be easily reduced to Siemens units by means of these numbers.

A train of wheels like that used by Feddersen †, which were set in motion by a falling weight, served me as apparatus for rotating the mirror. A vertical axis, to which two light plane mirrors were attached, could be rotated by it with a velocity reaching 100 revolutions in a second.

With the electrical tensions produced by a large number of elements, all parts of the circuit must be carefully insulated

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* Pogg. *Ann.* cvi. p. 554, 1859.

† Ibid. cxiii. p. 437, 1861.

from the earth. I generally used glass for insulators, which was coated with a layer of varnish.

The apparatus was arranged as follows:—One side of a wall which divides two rooms of my laboratory and contains a door, served for fitting up the 1600 cells, which formed two rows one above the other. The wires joined to the poles of the battery and covered with gutta-percha passed to the other side through holes in the wall lined with glass tubes. A table was fixed to this side, on which the greater part of the apparatus was placed. This room contains two stone slabs built upon the arched roof of the basement. The one immediately in front of the table was used for the telescope with a scale, as well as for the spectroscope (*Spectrometer*) and cathetometer; the galvanometer stood on the other, which is at the distance already mentioned. The connecting wires of the latter ran under the ceiling of the room up to the binding-screws of the rheostat over long glass tubes, coated with shellac, and fastened into the walls.

§3. The glass tubes which were used in the experiments to be here described, were of the shapes and dimensions represented in Pl. III. figs. 2 and 3. The electrodes consisted of aluminum wires 2 mm. thick, which projected 45 mm. into the tube and were at a distance of 50 mm. from each other in the interior of both tubes. The capillary of the one was about 15 mm. long. I do not fuse the electrodes into the glass, but, as in the experiments in my first communication, cement them in with fine sealing-wax. Small cylindrical tubes 4 to 5 mm. wide always form the ends of my tubes, through which the wire projects, and in which it is surrounded by a second closely fitting narrow glass tube. The latter always projects to a small extent into the wider tube. Liquid sealing-wax forced in by suction surrounds the extreme ends of the wire and tube for a long distance, and forms after cooling a perfectly tight joint, easily made or removed. When the powerful currents of the immersion-battery, which heat the kathode considerably, are used the corresponding terminal tube is surrounded by a wide vessel with water which, if the current passes for a considerable time, is continually renewed.

I will here observe that the electrodes of tubes with rarefied gases which contain narrow parts like the capillary tubes mentioned above, must not be directly connected with the poles of the immersion-battery by copper wires. The rise in temperature which is produced in the gas by using a large number of elements cracks the glass. By introducing one of the resistance-columns and regulating the distance of the cadmium plates, any desired diminution can be obtained.

The above glass tubes were connected with the mercury-pump, and contained hydrogen under a pressure of 8 mm. of mercury. The narrowest resistance-column (I) was introduced. The current generated by 800 cells, which was used for both tubes, became discontinuous when the distance between the cadmium disks exceeded 150 mm., that is, when the resistance introduced was more than 3,500,000 Siemens units. The images formed by the stratified positive light of the capillary tubes, appeared in a darkened room to be separated by dark intervening spaces and not perceptibly elongated. The dark intervening spaces were larger the longer the column of the solution of cadmium iodide. The light of the wide tube (Pl. III. fig. 2) behaved similarly when it fell upon the mirror through a narrow slit. The above resistance, which in this case is the limiting value for the transition from the discontinuous to the continuous discharge, was the same for both tubes. When the cadmium disks were not so far apart, the reflected light formed a continuous band, however high the velocity of rotation of the mirror.

When the light of the tubes appeared constant in the rotating mirror, the current caused a deflection of 8 mm. in the galvanometer when 2 × 96 cm. of the rheostat-wire were in the circuit. Its intensity was therefore only $\frac{1}{3840}$ of the maximum current furnished by the immersion-battery of the given dimensions. The relation of the limiting value of the resistance and strength of current to the length and density of the column of gas used, and to the electromotive force of the battery, can only be discussed later. I will only mention here that it does not vary appreciably if the pressure of the hydrogen gas is between 8 and 2 mm. The example given is at present only intended to show that the brush-discharge can always be obtained within wide limits by the above methods.

This at once shows why Gassiot did not obtain a continuous brush-discharge with his rain-water battery. For a single cell constructed with distilled water and with amalgamated zinc and copper in the form of cylinders, which were 55 mm. high and 35 and 19 mm. diameter respectively, only deflected my galvanometer 9 mm. when it, together with the length of wire mentioned above, formed the outer circuit. This element corresponds to the one used by Gassiot, so far as can be gathered from his communication *, which does not state the dimensions †.

The Holtz machine is still less able to furnish a continuous glow-discharge. In the one at my disposal, made by Ruhmkorff, the rotating disk has a diameter of 55 cm. If 10 Siemens units be introduced as metallic connexions between the combs, and the wires of my galvanometer are shunted from this, I only obtain a deflection of 18 mm., with as rapid a rotation as is possible without injury to the disk ; if 100 Siemens units are used, the deflection is 180 mm. The maximum current of this source of electricity is therefore only $\frac{1}{8}$ that of the above limiting current.

Rosetti's work ‡ has demonstrated that the current of the influence-machine follows Ohm's law just like that of every other known source of electricity. The independence of the intensity of the external resistance assumed by Gauss for the current of the frictional electrical machine, and by Poggendorff for that of the Holtz machine, is only an apparent one, and is due to the great internal resistance which here exists. The strength of the current diminished considerably when Rosetti introduced long and narrow tubes of distilled water. I obtained the same effect by shorter columns of amyl alcohol, which is a worse conductor. G. Wiedemann always used the current of a Holtz machine in his researches on

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* Phil. Trans. p. 39, 1844.

† Shortly before sending in my communication I found a short notice in the *Fortschritte der Physik* for the year 1863, according to which Gassiot subsequently obtained a continuous discharge in rarefied gases by means of a battery of 3360 cells, consisting of zinc, copper, and a saturated solution of common salt. The original communication (Proc. Roy. Soc. xii. p. 329, 1863) is not in our library, and was therefore inaccessible to me. Even in England this later statement of Gassiot also appears to have remained unnoticed. Compare Gerland in the Report on the Scientific Apparatus in the International Exhibition, p. 95. (*Vide* also Wiedemann, *Galvanismus,* ii. 2, § 967.)

‡ Pogg. *Ann.* clvi. p. 507, 1875.

electrical discharges in gases. He could not, therefore, determine the resistances of his gas tubes and their dependence on the dimensions, since they virtually disappear in comparison with the internal resistance.

The direct current (that is, the current on opening) of the Ruhmkorff coil, with which I obtained the results given in my first communication, is a much more productive and favourable source of electricity. Each induced current lasts an appreciable time, and when passing through the rarefied gas in the above tubes displays a broad continuous band in the rotating-mirror. The phenomena alluded to in my first communication, which for the most part could not be obtained with the feeble current of the influence-machine, were very marked when using a voltaic circuit; this, the most fertile of all sources of electricity, enabled me, as I had expected, to investigate these phenomena more exactly and quantitatively.

I have already mentioned that the apparatus at my disposal did not allow of my increasing the number of rotations of the mirror much above 100 per second, without endangering the stability of the axle. I do not doubt, however, but that a mirror rotating ever so fast will confirm the above result. I am primarily convinced of this from a phenomenon which always appears as soon as the discharge becomes discontinuous. On touching the tube with the hand the luminous gas is deflected by induction and is altered in shape, whereas during the steady discharge it remains quite indifferent when so treated. With a little practice it can be directly observed from the light whether the current is constant and continuous. The number and position of the positive layers, as well as the dark space, then remain quite unchanged. With a discontinuous current the appearance of the tube frequently changes. The dark space is sometimes larger and sometimes smaller, and the positive light often shoots out so as to almost touch the kathode.

In the discontinuous gas-discharge, produced by the immersion-battery when larger resistances are introduced, we evidently meet with partial discharges of the charged conductor which exists in the circuit on both sides of the column of gas. The electromotive force of the battery cannot replace the loss in the conductor in the time during which the single partial discharge is taking place in the gas, owing to the small coefficient of conductivity of the cadmium iodide solution. If the capacity of this conductor be increased, especially if a condenser be introduced, then, in order that the light of the same column of gas shall again give a continuous band, the resistance of the cadmium iodide solution must be further diminished. The separate images are formed in this case from successive spark-discharges of the condenser. The behaviour of this latter is most apparent when the discharge is continuous, and is of great interest in many ways.

I used a paraffin condenser for these experiments, such as has often been employed of late by English physicists. Thick unsized printing-paper, which had been heated to 200° C. in order to drive off its hygroscopic water, was passed, whilst hot, through melted paraffin. Two such paraffined sheets formed the dielectric between successive strips of tinfoil, which were arranged on a surface 42 cm. long by 30 cm. wide, and projected alternately at opposite sides in the usual manner. These projecting pieces of tinfoil were rolled over a glass tube and held together by means of a suitable metallic binding-screw. A single sheet of paper could not withstand the tension of my 1600 cells, and was perforated with sparks. The sheets lay firmly pressed together between two covers.

The arrangement of the experiments is represented diagrammatically in Pl. III. fig. 4, and will be intelligible without further explanation. I have only to remark that the four circles *a*, *b*, *c*, *d* represent cups of mercury carefully insulated. They can be connected with each other in different ways by means of insulated copper wires, and thus render the following combinations possible :—

If *b* is connected with *d* alone, the condenser is cut out. The cadmium disk in the resistance-tube can then be easily adjusted so that the light in the rotating-mirror just appears continuously. If, now, the connecting wire *d c* be used, the condenser becomes charged, and discharges itself through the column of gas, and the light again becomes discontinuous to a very high degree. The discharges take place more slowly in the tube the greater the number of sheets of tinfoil and the longer the resistance-column. By gradually pushing the positive cadmium disk down they follow one another with increasing rapidity. The light in the mirror suddenly appears again constant when the resistance has been sufficiently diminished.

If the condenser and battery consist of a larger number of sheets of tinfoil and cells, then the light caused by each discharge in the column of gas is no longer that of the brush-discharge, but has the appearance so well known in the Leyden jar. The stratification, the dark space, and the negative glow-light are wanting ; a continuous mass of light fills the space between the electrodes and terminates at the kathode in single bright metallic sparks. We shall dwell on this later.

The characteristic light of the brush-discharge again appears in the rarefied gas in proportion as the shortening of the resistance-column only allows a smaller and smaller fraction of the charge of the condenser time to discharge through it. The same is also true for the limiting case in which the light has become continuous. The condenser then no longer discharges itself, but remains charged with the difference in tension of the electrodes of the luminous gas, just as if it were at the ends of a metallic conductor. This is easily demonstrated by removing the conductor *c d* and making the connexion *a c*. A bright spark at the surface of the mercury marks the commencement of the discharge of the condenser. The difference in tension retained by the latter after the light has become continuous is not sufficient to cause a discharge in the tube when the gas is in its normal condition. This is shown by removing first of all the conductor *c d* and then *b d* during the continuous passage of the current. The battery-circuit is in this way totally broken, but the condenser remains charged. If the connexion *b c* be now made, the latter does not discharge itself through the column of gas, which remains dark. If the connexion *b d* were removed first, the condenser would naturally become charged with a difference of tension sufficient to discharge itself through the column of gas.

The moment at which the discharges of the condenser cease and the current becomes continuous in the gas is not apparent to the eye only, the ear too is conscious of it. A peculiar hard (*trockenes*) sound, proceeding from the condenser, accompanies each discharge, and is more apparent the greater the quantity of electricity of each single discharge. When the resistance is sufficiently small, the partial discharges, which follow one another at equal intervals in quick succession, give rise to a note whose pitch determines the number of discharges in the unit of time. The vibrations of the condenser cease as soon as the light in the tube becomes continuous.

Noticing the vibration in the condenser for the first time, I thought I had discovered a perfectly new fact. On looking up the literature, however, I found that Foucault in 1856 and W. Thomson in 1863 * had already observed it. The latter cited it correctly as a striking proof of the accuracy of Faraday's view as to the function of the dielectric. In 1866, Govi †, whilst charging a Leyden jar, noticed an increase in its internal volume, which immediately disappeared on discharging it. Duter ‡, in Jamin's laboratory, is at present investigating this phenomenon, and has already shown that this increase in volume is caused by an expansion of the glass.

The reason that the sound is not noticed in a Leyden jar under ordinary conditions is only due to the fact that it is masked by the report caused by the spark of the discharge in the air. On replacing the paraffin condenser by three large Leyden jars they vibrated audibly.

Up to the present I have only been able to turn my attention casually to this change in the dielectric of the condenser. In the above arrangement I noticed that the sound only accompanied the discharge of the condenser, and did not occur during the charging. I soon discovered the cause of this in the fact, that in the former case the change in the dielectric takes place quickly, since there is no such resistance as the cadmium iodide solution in the circuit. By introducing the widest tube (IV) between the cups *b*, *d*, I was able to make the sound as faint as I pleased, and finally inaudible by increasing the distance of the cadmium disks. The same sound is also apparent on charging the condenser, provided the resistance introduced be made sufficiently small.

It is worthy of note that if the glass side of the luminous gas tube be touched externally by the hand, it causes a change each time in the note given out by the rapid succession of partial discharges in the condenser. The interruption caused by the inductive action, and apparent to the eye in the change of appearance of the stratified light, is in this way also perceived by the ear.

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* Reprint of Papers, p. 263, 1872.

† *Compt. Rend.* lxxxvii. p. 857, 1878. ‡ Ibid. lxxxvii. p. 828, 1878.

On attempting several times in succession to determine the length of the resistance-column for which a given condenser remains charged with the same number of cells, it is soon noticed that it cannot be exactly determined in this way, and that it varies considerably. If the current has become continuous, it is possible, supposing that no interruption takes place, to again considerably increase the length of the cadmium iodide solution without causing the constancy of the light to cease or the sound to commence. The current is, of course, considerably weakened by this means and the intensity of the luminosity diminished. The condenser, however, remains charged until the resistance reaches a certain amount, when suddenly the discharges take place with the sounds above described. In order that these may cease and the current again become continuous, the resistance-column must be considerably shortened, as at first.

In order, therefore, to obtain the greatest amount of resistance at which the condenser no longer remains charged, the current must be first allowed to become continuous, and the movable cadmium disk of the cadmium iodide solution be then pushed slowly back until the sound and the discontinuity of the light commence.

This latter value depends primarily on the electromotive force of the battery when the column of gas remains the same. The capacity of the condenser is of relatively small effect. By gradually raising the number of sheets of tinfoil from 2 to 48, with a battery consisting of 1000 cells, I was able to increase the length of the cadmium iodide solution (III) up to 800 mm. by slowly and carefully pushing back the cadmium disk, before the continuity of the current in the gas ceased. If the condenser consisted of 100 sheets of tinfoil, the largest number at my disposal, it was possible to increase the length of the resistance-column to about 600 mm. If the resistance exceeded this amount, the single discharges took place at a very slow rate with the condenser of larger capacity, each accompanied by a sound which here gave the impression of a blow of no inconsiderable force.

The gas used in these experiments with the condenser was hydrogen under a pressure of 5 mm., contained in a cylindrical glass tube, 8 mm. wide, of the shape represented in Pl. III. fig. 5. The kathode was a thin iron tube, 3 mm. in diameter and 30 mm. long, fastened to a wire surrounded by and projecting from a glass tube. A disk of aluminum formed the anode, which was placed at the straight end of the tube at a distance of 68 mm. from the other. The wire connecting it passed through a capillary tube, to the side of which a smaller one was fused, provided with a very small Geissler stopcock. The latter was used for rarefying and filling the tube by means of the mercury-pump.

The remarkable behaviour of the condenser alluded to is owing to the fact that its charge remains almost constant in spite of the great alterations in the strength of the current passing through the column of gas, which are caused by moving the cadmium disk in the resistance-tube. This is noticeable in discharging the condenser. For if the connecting wire be taken out of the cups *c*, *d*, and placed in *a*, *c*, whilst a continuous current is passing through the column of gas, no difference is observable in the strength of the spark formed at the surface of the mercury by the discharge of the condenser, however variable the strength of the current. I have verified this relation more exactly by passing the charge of the condenser through the galvanometer, and observing the first deflection of the magnet. For this purpose two mercury-cups *f*, *g*, were arranged in addition to the four insulated ones *a*, *b*, *c*, *d*, and connected by a circuit containing the whole length of the narrowest resistance-column (I) as well as a long German-silver wire stretched over glass tubes. The wire of a mirror-galvanometer was shunted from the latter. The column of gas consisted of hydrogen under a pressure of 3 mm.; it was contained in the glass tube (Pl. III. fig. 5), and always shut off by the small glass tap. The connecting wire *c d* was removed when the light of the glow-discharge had become continuous and the condenser no longer emitted sounds. The connexions between the cups *a f* and *c g* were made immediately afterwards by means of two wires fastened to the same glass rod and insulated from one another, and caused the discharge of the condenser through the circuit already described. The results are arranged concisely in the following table. The condenser consisted of 12 sheets of tinfoil. 1200 cells were used, the zinc rods of which were very short.

Length of the resistance-column (III) interposed.	Deflection of the galvanometer shunted by 2×50 cm. of the rheostat-wire.	First deflection from the charge of the condenser.	The glow-light covered the kathode to a distance of:—
millim.	millim.	millim.	millim.
30	510	100	30 (totally).
132	122	98	25
350	46·5	88	10
730	21·5	84	5

The strength of the charge in the condenser was between 84 and 100, whilst the intensity of the current in the column of gas varied from 1 to 24. The deflections caused by the former would have been quite constant if the length of the column of gas, which is part of the conductor of the current, had remained unchanged. This, however, was not the case. With strong currents the negative glow-light covered the whole length of the iron tube, and its extent decreased continuously with the strength of the current, as shown in the last column. We shall allude to this later when investigating the phenomenon of the negative glow-light.

If the column of gas in the above series of experiments be replaced by a metallic or electrolytic conductor, then, as is well known, the difference of potential of its poles, and therefore the charge of the condenser, is proportional to the strength of the current. The conductivity of the column of gas cannot, therefore, have remained constant like that of the conductor, but must have changed proportionately with the strength of current, since the difference of tension remains constant. This fundamental relation for the conductivity of a gas will be proved directly in § 9 and its signification investigated.

In these determinations, and in all measurements arranged for studying the conducting-power of gases, a source of error must be borne in mind, which up to the present I have not succeeded in removing. All metals contain occluded gases, and this is more especially the case with aluminum, which is difficultly volatile, only volatilizes through the hot stratum of the glow-light under the influence of very strong currents, and thus serves admirably as the kathode. Graham's and H. Deville's researches have shown that these gases consist more especially of hydrogen and carbon monoxide. They are liberated to a greater or less degree in spectrum-tubes with metallic electrodes when the kathode becomes heated by the current, and are the cause of the lines of the former gas and of what are called the flutings of the latter which appear in the spectrum of each gas, however pure it may have been originally. The cause of this well-known fact is not the moisture of the gas or the grease from the stopcock, as had been assumed previous to Graham's work. I have already spent much time and trouble in preparing electrodes free from gas for this research, and I shall continue these investigations, as the exactness of the measurements depends so essentially upon them. I, as well as other physicists *, have up to the present not succeeded perfectly by Graham's method, which consisted in maintaining the metals for a long time at a moderate red heat in a vacuum. What is really required for these experiments is a metal which is incapable of occluding gases. For metals, so long as they possess this property, though they have been entirely freed from gases, do not fully satisfy the requirements of the case, as they sometimes absorb and sometimes exude gas, according to the temperature produced in the kathode by the current, and in this way alter the mass of the gas, which ought to remain constant.

The extent to which this has taken place must be determined in all quantitative measurements. In order to effect this in all measurements, the glass tubes, as represented in Pl. III. fig. 5, were cemented by the capillary tube to the tube of a barometer, by the side of which a second one of the same diameter was placed. (*Vide* Pl. III. fig. 6.) Both barometers stand in a glass vessel containing mercury and provided with a tap, and communicate with the mercury-pump by capillaries and glass taps. When the taps are closed, after the same tension of the gas has been established everywhere, it is possible to determine whether occluded gases have been liberated from the kathode by the current. If this has been the case, the level of the mercury in that particular barometer will fall below that in the other, when the taps are opened after breaking the current and allowing the tubes to cool.

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* Beetz, Wied. *Ann.* v. p. 4, 1878.

Up to the present I have, to some extent, tried to overcome this drawback by employing, for some time before the experiment itself, a much stronger current than that which I purposed using, so that the kathode was more strongly heated than afterwards and evolved a part of its occluded gas. The tube was then completely exhausted, again filled with gas, and the experiment itself commenced with a weaker current. I only considered the result of the experiment as available if the gas afterwards had retained its tension unaltered. If this were not the case the experiment was repeated in the above manner.

More recently I have found it advisable to make the kathode of a thin metallic tube, as already alluded to above, for in this way occluded gases can be more easily removed by strong currents.

§4. Having shown in the experiments in the preceding paragraph that the spark can be made continuous by means of our most productive source of electricity, a chemical process, we have obtained those conditions favourable for the experimental investigation of the conduction of gases which Carlisle and Nicholson obtained at the commencement of this century as regards electrolysis, by observing the decomposition of water in the circuit of the voltaic pile. The appearance of the constituents of the electrolyte at separate poles was entirely unknown to the physicists of the last century, who only had at their disposal that feeblest of all sources of electricity, friction, with its weak discontinuous chemical actions, in spite of the fact that Van Marum studied these latter with his large electrical machine. Similarly the so essentially different character of the phenomena of light and heat which occur in the glow-discharge was up to the present not sufficiently recognizable in the currents from the electrical machine and induction-coil. It is, however, immediately apparent by using the continuous discharges of the galvanic current. If, namely, the resistance introduced be still large but the light already continuous, the latter, however long continued, when filling also the whole diameter of the tube, and even extending into the capillary parts, warms the glass so little that the rise in temperature can be borne by the hand without inconvenience. The intensity of the continuous light appears in wider tubes just as great in the centre, as in those parts of the glass side directly touched by the luminous particles of gas. The same applies to the surface of the anode, however good a conductor be the metal of which it is formed. And yet the strong cooling would produce considerable differences if the positive light were accompanied by a high temperature. The inner surface of the glass in the capillary is first of all attacked by the brightly luminous hydrogen ; but a yellow coloration due to sodium vapour, and black specks of reduced silicon do not appear there until the strength of the current exceeds by more than one hundred times the value at which it becomes continuous. Such a current must only be allowed to pass momentarily, for after a short time the glass becomes so hot that it cracks. We shall see afterwards that the stratum of gas in the negative glow-light, immediately surrounding the kathode, behaves quite differently, and generally appears dark in spite of its high temperature.

All doubts as to the character of the positive light in the glow-discharge are removed if the current is passed through the rarefied gas in a cylindrical tube 8 mm. wide, represented in fig. 5, Pl. III., while the latter is attached to a barometer-tube in the manner mentioned at the conclusion of the preceding paragraph. By introducing a suitable resistance, the current can be so adjusted as to be continuous, and to cause a luminosity throughout the whole section. The whole amount of gas, with the exception of the dark space in front of the kathode, will appear luminous if both the electrodes consist of metallic disks, and are close to the straight glass sides. If during the steady passage of the current one tap is open and the other closed, it is possible to observe the temperature, as in an air-thermometer, by means of a kathetometer, from the change in pressure shown by the height of the column of mercury. If the kathode gives off no vapour, stronger currents are necessary to cause a distinct depression of the mercury. This is partly due to the high temperature of the dark stratum of the negative glow-light, which will subsequently be referred to. The temperature of the particles of gas which radiate positive light is here not very different with constant currents from that of the inner surface of the glass. This entirely corresponds to the known behaviour of gases, namely, that they rapidly assume the thermal state of bodies with which they are in contact, owing to their small density and the great mobility of their particles. I have often suspended little strips of the thinnest paper for a long time in the positive light of wider tubes, but could not observe the smallest trace of carbonization.

Plücker and I committed therefore a great error in our joint work on the double spectra of gases * in assigning very high temperatures, mostly exceeding those of our hottest flames, to the gas particles which give spectra of the first order. This error arose chiefly from the fact that only a small number of spectra were obtained with the hot test flames, which were identical with electrical spectra of the first order. This is the case with the vapour of sulphur, as stated in that paper, and subsequently confirmed by Salet † and others. Its electrical spectrum coincides with that given out by it when burning in oxygen. A sulphur flame burning in air only gives a faint continuous spectrum. The same is the case with selenium. Similarly, gases containing carbon give the same groups of lines as those to be observed in their flames, and which appear so bright, especially when fed with pure oxygen. Now as we did not find the spectrum of nitrogen of the first order in any flame burning in air, nor in a cyanogen flame fed with oxygen, and as we further had looked in vain for the characteristic lines of hydrogen in the oxyhydrogen flame, which on the other hand were already recognized as among the most important of the dark Fraunhofer lines, we came to the erroneous conclusion that higher temperatures were necessary for these electrical spectra, which only the electrical discharge could produce.

In the numerous researches which have since been made

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* Phil. Trans. 1865, p. 1.

† *Ann. de Chim. et Phys.* [4] xxviii. p. 1.

on electrical spectra with the aid of the induction-coil, our conclusion, so far as I am acquainted with the literature, has, up to recent times, been accepted by authors. Only Kirchhoff in his classical treatise* had indicated the correct view. He says there, p. 276 :—

"Each body emits rays the quality and intensity of which are dependent on its nature and temperature. Under certain circumstances other rays can be superadded to these; this is, for instance, the case if the body is electrified to a certain degree, or if it phosphoresces or fluoresces. Such cases are here excluded. If the body is struck by rays from without, it absorbs a part of them and changes it into heat. Under certain conditions another absorption occurs, which is the case, for example, if the body is an absorbent of light or if it fluoresces. It is here assumed that all the rays absorbed are converted into heat."

And, p. 295 : "The spectra which other salts produce, when introduced into a flame, are generally less simple and seldom give lines as bright as those of lithium. It must, however, be possible in a similar manner to invert all these spectra : if the flame be made of the requisite thickness and if light of sufficient intensity be passed through it, the lines which previously were bright must be transformed into dark ones. An exception could only occur in the case of a flame in which part of the light was caused spontaneously by a chemical process or in a flame which fluoresced. Experiments must decide whether there are such flames."

Only within the last few months has a doubt been expressed as to the high temperature of luminous gases. Spörer, in the November number of the Memoirs of the Berlin Academy, describes some singular forms of protuberances which are separated from the body of the sun by dark spaces, and contends that the origin of their light is due to a chemical process. E. Wiedemann too, in the February number of the *Annalen*, comes to the conclusion, from measurements of the heat caused by the induction-current in a capillary tube, and taking into account a relation discovered by his father, that the particles of gas, which were uniformly luminous in the parts of the tube 3 cm. wide he used, must have had temperatures below 60°. This latter statement obliged me to collect and publish my extended observations and measurements, although I would gladly have completed them.

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* Pogg. *Ann.* cix. p. 275 (1860).

The constant currents, which the galvanic battery enables us to produce in gases, leave no doubt that spectra of the first order have the character of phosphorescent light. All non-metallic gases, whether elementary or compound, can probably be put into a phosphorescent state by means of the electrical current, and therefore possess a spectrum of the first order. In many cases this is only a continuous one, and therefore not characteristic. The galvanic battery is the best source of electricity for obtaining these spectra and investigating them exactly, for with it, electromotive force as well as resistance can be varied at will. The spectrum research which Plücker and I carried out with the aid of the induction-current require to be supplemented by using a galvanic current, and the results of this I shall reserve for another communication. I confine myself here to the discussion of the phosphorescent spectra of two important gases, nitrogen and hydrogen, which may serve as examples.

The gradual increase in the strength of the positive light and of its spectrum is a beautiful phenomenon, which makes its appearance in the spectrum tubes (Pl. III. fig. 3) when the column of cadmium iodide solution in the circuit is gradually diminished, the number of cells being sufficiently large. If the contents of the tube consist of air or nitrogen, numerous fine lines of the well-known spectrum of the first order become more and more distinct and individually defined. The whole colour of the luminous thread of gas becomes whiter and whiter. The brightness is dependent on the density of the current, and is therefore greater the narrower the section of the tube. If there is no resistance besides that of the column of gas and a larger number of elements is used, then the simultaneous rise in temperature in a capillary tube, as already mentioned, is so great that it splits the tube into countless fine cracks a few moments after closing the current. If the current be only allowed to pass for a moment, by introducing a mercury cup into the circuit and interrupting the current by rapidly immersing and removing the connecting wire, it is possible to observe the most brilliant spectrum my immersion-battery can produce. This was still of the first order, even when using a capillary of only $\frac{1}{2}$ mm. diameter. No lines of a spectrum of the second order were apparent. In order to obtain the latter a condenser is indispensable.

The modifications which take place in the spectrum of hydrogen, according as the density of the current varies, are of still greater interest. If a wider tube (4 to 9 mm.) be placed in front of the slit then, with pressures of 2 to 8 mm., as soon as the resistance introduced is sufficiently large, a spectrum is obtained which shows only a single faint green line. Bands of carbon monoxide due to the electrodes generally accompany it. On decreasing the resistance there appear first of all, in addition to this green line, whose intensity increases, two yellow lines which are about three times as distant from one another as are the sodium lines. I must reserve the exact determination of the wave-length for a future communication. If the resistance be still further diminished, numerous well-defined lines appear in the red and yellow parts of the spectrum, to which we called attention in our communication in 1865, without, however, giving a drawing. Wüllner * supplied it subsequently. It has been stated that Paalzow and H. W. Vogel †, have photographed this spectrum. The current now need only be slightly increased in strength in order to obtain H_α, H_β, and H_γ in addition to the above lines.

This complete phosphorescent spectrum of hydrogen was first found in a tube 9 mm. wide, with a tension of 4 to 5 mm., when the deflection caused by the current in the galvanometer was about 100 mm., the latter being shunted by 2 × 10 cm. of the rheostat wire. The narrower the tube and the smaller the density of the gas, the weaker the current necessary to produce it. The same spectrum is also obtained with capillary tubes when the resistance-column is removed and the current is made discontinuous in order to prevent fracture. In that case, however, H_α, H_β, and H_γ exceed the other lines in

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* Text-book, ii. pl. iv.

† *Berichte d. deutsch. chem. Ges.* xii. p. 334 (1879).

intensity. The latter disappear and the former become wider when the condenser is interposed.

In harmony with the phosphorescent character of these spectra is the fact that the bright lines cannot be inverted, although their light is continuous. I have convinced myself of this by employing a luminous column of hydrogen 3 cm. long and 4 mm. wide. The glass tube containing it was closed at both ends by parallel glass plates, and its electrodes were inserted in two tubulures fused in the sides. Light from different solid bodies, raised to a strong red heat, was passed in the usual manner through the gas, which was rendered luminous by currents of different intensities. The inversion of the four hydrogen lines H_α, H_β, H_γ, and h, which takes place in the sun, is probably only possible at the high temperature of the deeper layers of the solar atmosphere. It is certainly noteworthy that in the case of hydrogen, lines which are already contained in the phosphorescent spectrum also appear at temperatures at which the gas itself is luminous, whereas with nitrogen other and totally new lines appear. I intend to refer to this in a separate communication.

§ 5. The sources of phosphorescence, that is, of luminosity at a low temperature, known and employed up to the present have been friction, chemical action, and irradiation. That friction can excite phosphorescence and cause luminosity at temperatures below a red heat, is shown in the case of substances which cannot undergo a red heat without chemical decomposition. Cane-sugar, as is well known, and a number of other organic compounds become covered with a faint glow at the places rubbed, which is only visible in the dark. Uranium nitrate, when crystallized from water ($Ur(NO_3)_2+3H_2O$), forms another example of this; the crystals when powdered in the dark shine brightly, but after removing their water of crystallization by gentle heating they no longer emit light.

Luminosity at a low temperature due to chemical action has long been observed in the slow combustion of phosphorus, and has given rise to the nomenclature in use. Slow oxidation effects a similar feeble disengagement of light in many organic compounds—sulphur, potassium, sodium, and others. The phosphorescence shown by certain animals and plants is doubtless due to the same cause.

Up to the present irradiation has been the method most generally used for obtaining the phenomenon of phosphorescence. Our present knowledge is chiefly due to it. In solid bodies, moreover, it causes a peculiar permanent change in the molecules struck, which manifests itself in the fact that when the after-luminosity has entirely ceased at a certain temperature it can again, by warming the body, be caused to appear for a longer or shorter time. After the substances have ceased to emit light, and have cooled in the dark, phosphorescence does not recur if they again be raised to the same temperature. To cause this to take place they must be irradiated afresh. Thus, heat only acts in a secondary manner ; it cannot be considered as one of the primary sources of phosphorescence. Kirchhoff also holds this view, for he expresses himself as follows in his investigations on the solar spectrum[*] :—

"Draper has been led by experiments to the conclusion that all substances begin to emit light at the same temperature. He has, however, noticed in his experiments that certain substances, for instance lime, marble, fluor spar, become luminous at lower temperatures than they ought to in accordance with this law ; he calls this luminosity phosphorescence, and states that it distinctly differs in colour from incandescence. This luminosity, by whatever name designated, is in contradiction to the principle laid down in § 3, and a substance which shows it cannot satisfy the assumption made in proving this theory—it cannot remain unchanged the temperature remaining constant. Phosphorescence is not a mere action of heat, it is not dependent solely on the temperature, but is caused by changes in the substance ; when these changes have ceased, whether their nature be chemical or otherwise, then the phosphorescence must also disappear."

If the molecules during irradiation be heated, the after-luminosity is much more marked. I have convinced myself of this in the case of the best phosphorescents, the sulphur compounds of the metals of the alkaline earths, by strewing them in fine powder in a dark room on a piece of thin platinum foil, placed horizontally, which could be heated by means of a galvanic current. If the powder had been struck by ordinary daylight, which had previously passed through two superposed glass plates, the one coloured with manganese and the other with cobalt, and had thus lost the less refrangible rays, the yellow phosphorescence was very marked each time on closing the current. The increased luminosity soon ceased when the rise in temperature had become constant. If the latter were increased up to the point at which the powder began to glow, the phosphorescence disappeared entirely.

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[*] *Abhandlungen der Berliner Akademie,* p. 38 (1861).

The distinction which Stokes made between phosphorescence and fluorescence, and which was principally based on the assumption that the latter only existed during irradiation and had no after-action, has, simultaneously with this assumption, been shown to be untenable by E. Becquerel's investigation. The latter, as is well known, was able to demonstrate in many fluorescent substances, by means of his phosphoroscope, a decided after-action of the luminosity.

The three methods alluded to cause so faint a luminosity at low temperatures that a dark room is usually necessary for observing it. For this reason I was formerly of opinion that phosphorescence could not possibly occur with such an intensity as is shown by the luminosity of molecules at a very high temperature. The negative glow-light showed me first of all that this conclusion was an erroneous one. Geissler has for a long time supplied glass tubes with rarefied gases and wire electrodes, which contain sulphur compounds of the alkaline earths, principally calcium sulphide, in powder or in small pieces. The phosphorescents can, by means of the induction-current, be caused to emit light which lasts for some time. If the powder is distributed over the whole length of the tube, and is thus in contact with the positive as well as with the negative light, a stronger phosphorescence is apparent in those particles which are struck by the latter. This difference is much greater if a glow-light be used generated by a strong induction-current at a kathode with a small surface in very rarefied gases. I use a tube of the shape shown in Pl. III. fig. 7. An aluminum wire (*c*) 2 to 3 mm. thick is surrounded by a glass tube in such a manner that only the terminal section is exposed inside the tube. A second thinner aluminum wire (*a*) is placed in the lateral part fused on to it. After powdered calcium sulphide has been placed in the tube, the latter is filled from the mercury-pump with air or hydrogen at a low pressure (about 0·5 mm.) and sealed up*. As I showed in my first communication, there are formed at the small cross section, if it is negative, very hot, slightly luminous radiant particles of gas emitting light of a high refrangibility, which extend straight through the whole tube (*mn*) and cause this to phosphoresce, although the anode is behind the section. The positive light emitted from the lateral wire (*a*) seeks to join these glow-rays. On reversing the current, the part of the tube (*mn*) is non-luminous. The positive light at the section of the wire (*c*) bends round and takes the shortest path to join the negative glow-light which surrounds the surface of the wire (*a*). If now the calcium sulphide be allowed to come into contact with the negative glow-light emanating from the cross section, the spots touched show an intense white luminosity which causes strong after-images in the eye when held near, and can even be distinguished in bright daylight. It gives a bright spectrum which appears continuous from red to violet, as in the case of a white-hot body. On breaking the current the intensity of the luminosity is immediately decreased to a considerable extent. The tube serves equally well for causing other substances to phosphoresce vividly. In this way all kinds of calc spar, which after insolation show a phosphorescence which can only be detected in the phosphoroscope, give out a yellowish-red light which is apparent in the dark for quite 10 minutes after the current has been broken. By working the medium-sized Ruhmkorff's coil, alluded to in my first communication, with more than two large Grove cells the glow-rays heat the surface of the calcium sulphide in several places to redness. These spots appear quite dark beside those which are brightly phosphorescent and less warm, and show that solid bodies at an incipient red heat can no longer phosphoresce.

This behaviour can be more strikingly demonstrated by arranging the experiment differently. The tube (Pl. III. fig. 7) was made of rather thick, very hard Bohemian glass. Glass of this kind softens so little at a dark red heat that it withstands the atmospheric pressure even when exhausted. It was thus possible, by means of two burners, to raise the part of the tube (*mn*), containing Canton's phosphorus, together with its contents to a dark redness. The powder in that case was unaffected by the glow-rays; it did not phosphoresce. At the boiling-point of sulphur (447° C.) phosphorescence was still apparent, but was of very short duration.

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* Three of these tubes were shown at the International Exhibition in London, 1876. *Vide* Biedermann, *Bericht*, p. 319, No. 1765.

All solid substances probably phosphoresce at the temperature at which they begin to emit red light, but no longer do so at what is called obscure red heat. Ordinary non-metallic gases behave differently. For many gases, when they are burned with oxygen, show spectra of the first order, which also appear at a low temperature in the circuit of the electric current. The light of our ordinary burners, which contains no solid particles, is not due to the temperature but to chemical action, and must be considered as a phosphorescent light. For if these same gases have acquired the temperature of the flame, without having taken part in a chemical action, they do not emit light perceptible to the eye. This can be demonstrated by suspending horizontally a piece of the thinnest platinum foil rolled into a cylinder with open ends, in the hottest part of a Bunsen burner with the air-holes opened to their full extent, and looking towards the axis of the cylinder in a dark room through a narrow tube in order to cut off the rays emitted by the glowing metal. The gas within the tube appears dark and different from that of the luminous flame. Gases in the interior of a tube made white hot in a coal-fire show a similar result.

It will moreover be proved in a subsequent paragraph that the electrical behaviour of gases in a flame is different from that exhibited by the same gases at the same temperature when not undergoing chemical action.

These facts are not opposed to the theory that all bodies begin to emit light of the same wave-length at the same temperature. Ordinary gases have, too, no appreciable power of absorption, and therefore also, according to Kirchhoff's law, they can have no such power of emission.

The immersion-battery, consisting of 1600 cells with no resistance interposed, is best adapted for observing the behaviour of ordinary gases at high temperatures. In order to avoid the great loss of heat which takes place with narrow tubes, a thick tube of hard glass, 35 mm. in diameter and 25 cm. long, was employed. Two brass wires 6 mm. thick were passed through the corks at each end, and terminated in the interior in platinum wires, which were at a distance of 20 to 25 mm. from one another (Pl. III. fig. 8). The upper platinum wire, which served as the kathode, was 4 mm. thick, in order that it might not fuse owing to the high temperature of the gas surrounding it. The lower wire could be thinner and had a diameter 1·8 mm. A cooling-vessel surrounded the negative brass wire, in order that the heat which it transmitted should not soften the sealing-wax employed for rendering the cork tight.

In this case again I shall confine myself to the behaviour exhibited by air and hydrogen. The current from the 1600 cells passed between the electrodes at the above distance if the air in the tube had a tension under 50 mm. If no resistance were introduced, then, on closing the current, the yellowish-red light still appeared at the positive and the blue glow-light at the negative pole. In proportion as the two platinums became heated, these lights soon disappeared altogether when the tension exceeded 15 mm. The evolution of heat in the stratum of gas surrounding the kathode was always considerably in excess of that surrounding the anode. If the platinum electrodes were raised to a white heat, a faint bluish light surrounded the anode, sometimes filling the space between the electrodes, and sometimes leaving a dark space in front of the kathode. This positive light gave an exceedingly faint continuous spectrum, in which none of the lines of the first spectrum of nitrogen could be distinguished. The lines of platinum vapour were also wanting; they were only present when the distance between the electrodes was less than 10 mm. The stratum of air surrounding the white-hot kathode to a distance of 10 mm. appeared quite dark to the eye, and could thus have no property of emission. Its temperature, however, must have been very high, for in spite of its small mass it caused the difficultly fusible metal to melt at the bottom, and thinner wires dropped like wax. It was not owing to the contrast with the bright light of the metal that any possible feeble luminosity of its particles was imperceptible. This was shown in the case of the adjacent positive light, which was visible in spite of its feebleness. As soon as the kathode became white hot, and the glow-light round it disappeared, no more metal volatilized from its surface; whereas it is a well-known fact that platinum deposits a strong mirror on the surrounding glass side during the continuance of this light.

The current from the 1600 cells which produced this condition in the particles of air, deflected the galvanometer 180 mm. when shunted by 2 × 2 cm. of the rheostat wire, and was thus about $\frac{1}{3{\cdot}5}$ of the maximum current. The condition continued if air were allowed to pass in slowly. It was possible to retain it when the tension in the interior was equal to that of the external air. The deflection of the galvanometer only changed slightly and fell to 165 mm. This behaviour is characteristic of strongly-heated gases; we will subsequently investigate it more closely. If a bad conductor of heat, such as gas-carbon, were used as the kathode, the current was still more easily continuous as the pressure increased.

The blue glow-light of the kathode disappeared, but not the yellowish-red positive light, if the air had a tension under 15 mm. On closing the current, the former covered the whole length of the wire within the tube, but contracted considerably in proportion as the platinum end glowed more strongly.

The arc-discharge could be prevented and the glow-discharge obtained at any desired pressure by sufficiently decreasing the strength of the current by the introduction of a resistance, thus rendering that high thermal condition impossible.

The behaviour of hydrogen in the tube was similar to that of air. The lines of the phosphorescent spectrum, however, alluded to above in the whitish positive tongue of light were still observable at greater pressures, and in a similar manner small spots of glow-light remained for a longer time at the extremity of the white-hot platinum. Both these, however, finally disappeared when the pressure was sufficient.

On allowing hydrogen to enter in slowly the strength of the current diminished considerably, and the current ceased when the pressure was about 550 mm. and the deflection had fallen to 65 mm. The greater thermal conductivity of hydrogen was apparent in yet another way. The tubes were originally made of soft glass. The hot hydrogen, however, heated the opposite side in spite of the considerable diameter, and caused it to soften so that it bulged inwards from the pressure of the air and a hole was pierced.

It is scarcely necessary to add that the glow-discharge remained constant in hydrogen if a sufficient resistance were introduced. The glow-light was also obtained without its help if the heating of the kathode was prevented by rapidly absorbing the heat imparted to it by the gas. For this purpose I employed as the kathode a thin copper tube closed at its lower end, with a glass tube in its axis through which a current of cold water could be passed. At low pressures the blue glow-light covered the whole surface, decreasing more and more in extent with the increase of pressure, until it diminished to a few square millimetres at the apex of the tube. It always contained numerous fine bright points, which consisted of copper vapour, and was so hot that the noise of incipient boiling commenced as soon as the water flowed somewhat slowly. The deflection from the 1600 cells in the galvanometer shunted as above was in this case 115 mm.

§6. The assumption founded principally on Coulomb's* experimental investigations is still accepted, that the electric charge of an insulated conductor is dispersed, not by the solid insulator alone, since in all cases this is a bad conductor, but also by the air in contact with it at the ordinary temperature. Coulomb expresses his view of this latter process in his memoir as follows :—

"The second cause is that the atmospheric air, composed of different elements, which surrounds the electrified body, is more or less ideo-electric, whether this be due to the nature of its elements or to the affinity of these for molecules of water ; which affinity changes also in correspondence with the degree of heat, so that air can be considered as composed of an infinite number of partly ideo-electric and of partly conducting elements. As, moreover, a conductor is always charged with a part of the electricity of the body in contact with it, and as after becoming charged it is repelled from the body, it follows from this that each molecule of air which touches an electrified body becomes more or less quickly charged with the electricity of this body, according as the density of the electricity of the body is greater or less, or the air is filled with more or less moisture or with particles conducting electricity. As soon as a molecule of air is charged with electricity, it is repelled by the electrified body and replaced by another which in turn becomes electrified and is again repelled. Thus each of these molecules conveys part of the electricity away from the electrified body which they surround, and its electrical density diminishes quickly or slowly according to the state of the atmosphere."

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* *Hist. de l'acad. roy. des scienc.* 1785, p. 612.

This view of Coulomb is based primarily on the assumption that aqueous vapour is a conductor of electricity, and a far better one than the other components of air at a low temperature. This assumption, which the electrical behaviour of the liquid state of a body challenges for the gaseous state, can in no wise be justified without further experimental investigation. For if the vapour of boiling water be allowed to pass through a lateral tubulure into a metallic tube open at both ends, connected with one pole of a galvanic battery, while a wire communicating with the other pole is placed in the axis of this tube, then even the most delicate galvanometer forming part of the circuit shows no deflection so long as the number of cells is insufficient to cause a luminous discharge.

That the conductivity of the fluid state is no criterion for that of the gaseous is very beautifully shown in the case of mercury, which when liquid is one of the best conductors, but in vapour is an insulator, like all gases, so long as the temperature remains below a glow-heat. A hard-glass tube about 20 cm. long, and closed at the bottom, has tightly cemented to its upper edge, by means of sealing-wax, a glass bell-jar with three tubulures (Pl. III. fig. 9). Two iron wires, surrounded to their ends by glass tubes, are firmly cemented into the two parallel vertical tubulures and form the electrodes. To prevent the sealing-wax from softening it is kept cold by means of a vessel with running water. An iron plate protects the latter from the hot ascending gases. The air can be replaced by hydrogen of any desired pressure through the third tubulure of the glass bell-jar by means of the mercury-pump. Mercury at the bottom of the tube can then be kept boiling by means of a burner. In proportion as the vapour is formed below, it condenses in the upper part, and falls down in fine drops on the inside wall. If the iron wires, of which the free ends are constantly in mercury vapour, are connected with the galvanic battery and the galvanometer, the latter is only deflected when the number of cells is sufficiently large to cause a luminous discharge, which displays a beautiful green light. This has quite the character of the glow-discharge if a sufficient resistance be introduced.

The contrary result obtained by Herwig * was owing to an incorrect arrangement of the experiment. Herwig heated one part of a glass tube filled with mercury so strongly that the vapour of the liquid metal kept dividing into two parts, which served as electrodes for the voltaic current. In this case, however, there was the hot conducting glass between the electrodes as well as the vapour of mercury. Herwig considered that the conduction due to the glass was small, because in the same tube and at the same temperature he had obtained much smaller deflections in the galvanometer by using the same current, and employing as electrodes two pieces of platinum foil, each surrounding a bundle of thin brass wires resting against the glass sides. Contact, however, in this latter case is much less complete than with a column of liquid mercury. The microphone shows what great diminutions in the strength of the current are caused by such faulty contacts. The rapid fall which occurs in these experiments in the deflections of the needle is not caused by an enfeeblement in the conduction of the vapour, but is due to the ions of the glass becoming separated. This is easily demonstrated by means of the inverse current which they generate.

Coulomb, in his determinations of the coefficient of leakage of the air, did not utilize any of the valuable drying sub-

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* Pogg. *Ann.* cli. p. 350 (1874).

stances which Chemistry furnishes us with, but carefully observed the amount of moisture by means of a Saussure's hygrometer. In referring to the results which he obtained with the torsion-balance he presupposes that both his electrified pith balls, of which the conductivity, as is well known, is only due to their hygroscopic water, suffer no loss through the rods of shellac. He justifies this assumption with the observation that the knobs in the same air, and during the same time, showed the same loss of electricity when they were supported by four rods of shellac instead of by one. The great influence of moisture is, however, unequivocally to be inferred from the numbers which he gives. The coefficients of leakage, for example, which he obtained with two masses of air, in which the amounts of water were in the proportion 2: 3, were $\frac{1}{60}$ and $\frac{1}{14}$ for the time of one minute. These coefficients, moreover, are exceedingly large if they are compared with the slow fall of an electrical charge in air which has been carefully dried by dehydrating substances, and can give up no water to the surface of its solid supports. Sir W. Thomson and other physicists have quoted numerous instances of this in recent times.

I used the following simple arrangement for my own information on this important point. A glass vessel (Pl. III. fig. 10), which could be connected with the mercury-pump, contains a long rod of shellac (*a*), with a brass wire at its lower end from which two gold leaves were suspended. The gold leaves can be charged without opening the vessel by means of a wire cemented into the hollow stopper ground into the lateral tubulure. The inner end of the wire terminated in a steel spring (*b*) which, by turning the stopper with the brass wire, could be brought into contact with the gold leaves. In this manner the latter could be electrified after they had been for some time in the vessel, which contained anhydrous phosphoric acid at the bottom. The loss of electricity could also be observed at any desired degree of rarefaction. If the gold leaves had been caused to diverge in an atmosphere of well-dried hydrogen at the ordinary pressure, by momentary contact with the pole of 200 cells, there could still be observed a small but distinct divergence after 4 × 24 hours, which immediately disappeared on contact with the steel spring which was connected to earth. The charge remained just as constant when the gas was greatly rarefied.

This knowledge in connexion with the whole electrical behaviour of gases leads me to accept Faraday's* view, that gases at a low temperature completely insulate low degrees of tension, and that the slow escape is only due to the solid insulator, a conclusion also shared at present by such English physicists as Maxwell †. According to a communication by Boltzmann ‡, Warburg has also accepted this view as correct, since he made by means of the torsion-balance § extensive investigations as to the escape of electricity in gases.

To decide this question by experiment we must leave a charged conductor without solid support in contact with gases only. According to an interesting communication by Reuleaux ¶, this now appears possible. During the Exhibition in Philadelphia in 1876, the beautiful experiment was shown of supporting a sphere by means of a strong current of air, like a jet of water, issuing in a slanting direction. In this case air perfectly free from dust and an electrified hollow metal sphere would have to be used, and the latter kept supported for a sufficiently long time.

§7. The process by which Coulomb, in the words which have been quoted, ascribes the leaking of the charge on the surface of a conductor to the surrounding particles of gas, takes place undoubtedly when the electrical tension at points reaches a certain amount. This latter, however, differs essentially from the former fictive one in that a luminous discharge, that is, a true electrical current, is formed at the extremity in the gas, even if only for a short distance. For the electrical wind is always accompanied by brush-light, which, however, on account of its faintness is only visible in a dark room.

Faraday first of all gave the correct explanation of the brush-light ‖. The electrical phenomena which are observed in gaseous media are only explicable if we consider them from the point of view of the theory of induction of the great English investigator. The scholastic theory of the electrical fluids becomes here still more unnatural than in the case of electrolysis.

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* Experimental Investigations, § 1336. Pogg. *Ann.* xlvii. p. 43 (1839).

† A Treatise on Electricity and Magnetism, i. p. 49 (1873).

‡ Pogg. *Ann.* clv. p. 415 (1875).

§ Pogg. *Ann.* cxlv. p. 578 (1872).

¶ Pogg. *Ann.* clix. p. 165 (1876).

‖ Experimental Investigations, §§1434–47.

I will call attention first of all to the important principle of Faraday:—

"517. *Judging from facts only*, there is not as yet the slightest reason for considering the influence which is present in what we call the electric current,—whether in metals or fused bodies or humid conductors, or even in air, flame, and rarefied elastic media,—as a compound or complicated influence. It has never been resolved into simpler or elementary influences, and may perhaps best be conceived of as *an axis of power having contrary forces, exactly equal in amount, in contrary directions.*"

The essence of the charge of two electrical conductors opposite to one another, separated by a gaseous medium, depends upon an induction or polarization condition of the molecules of this dielectric. This condition is produced by an electrical current of extremely short duration which is shown to be present, by well-known phenomena, in the adjacent conductors, and may in an analogous manner be assumed in all sections of the dielectric.

"All charge of conductors is on their surface, because being essentially inductive, it is there only that the medium capable of sustaining the necessary inductive state begins." (1301.)

The theory of the electric fluids generally received "refers the retention of electricity on the surface of conductors in air to the *pressure of the atmosphere* . . . .; and it associates two such dissimilar things, as the ponderous air and the subtile and even hypothetical fluid or fluids of electricity, by gross mechanical relations; by the bonds of mere static pressure." (1377.)

Faraday, in his classical researches on induction, showed that the same relation existed for the current, which causes the condition of polarization in the dielectric, as for that so well known in conductors.

"1634. Hence the section of a current compared with other sections of the same current must be a constant quantity, if the actions exerted be of the same kind; or if of different kinds, then the forms under which the effects are produced are equivalent to each other, and experimentally convertible at pleasure. It is in sections, therefore, we must look for identity of electrical force, even to the sections of sparks and carrying actions, as well as those of wires and electrolytes."

"Any section taken through the dielectric . . . . would be equal, in the sum of the forces, to the sum of the forces in any other section; and that, therefore, the whole amount of tension for each such section would be the same." (1369.)

Now the smaller the section of the dielectric at one point the higher will be the state of polarization of the individual molecules composing it, and the nearer will they be to the limiting case at which they can conduct and cause a discharge. But this is the case in the neighbourhood of a point. The luminous discharge takes place there as far as a certain section, where the molecules remain in the condition necessary for polarization. The latter therefore then fulfil the function which previously had been undertaken by the metallic particles at the surface of the conductor, and become charged. As, moreover, they are mobile to a very high degree, they experience mutual repulsion and attraction, and leave their position, which is then immediately taken up by other molecules, and these in turn experience the same lot.

The particles that are charged cannot communicate that state to their neighbours, the medium being a nonconductor. "They travel, therefore, under the influence of the repulsive and attractive forces, from the charged conductor towards the nearest uninsulated conductor, or the nearest body in a different state to themselves, just as charged particles of dust would travel, and are then discharged; each particle acting, in its course, as a centre of inductive force upon any bodies near which it may come." (1442.)

The same brush-light, as in an electrical machine, appeared in air of ordinary density at the extremities of fine wires when used as electrodes and sufficiently close to one another, when more than 800 cells of my immersion-battery were connected in series. This continuous discharge was extremely interesting to me on account of the change in the dark layers of the positive light, and I have therefore carefully studied it under new conditions.

Before communicating the results I must make some remarks as to the discharge of my battery between broad surfaces.

In my second communication I showed how the sparking distance of the battery could be very easily determined by means of the spherometer, and gave some of the measurements with the immersion-battery, which at that time consisted of 400 cells. De la Rue and Müller have recently made and published a large number of measurements with a chloride of silver battery of more than 8000 cells, using the same apparatus*. This renders a continuation of research superfluous for the present. When all the 1600 cells of my immersion-battery are connected, the latter has in air at the ordinary pressure a striking distance of about 1 mm. between the knobs of my spark-micrometer, which are 15 mm. in diameter. If no resistance be introduced, the arc-discharge commences, accompanied by a high temperature ; the metal of the knobs volatilizes and forms a good conducting medium for the current. On separating the electrodes a bright spark several centimetres in length, is obtained in the case of easily volatile metals, showing the spectrum of the metal. Between carbon electrodes the Davy arc is formed at the above distance of 1 mm. All these arc-discharges are feebler than those produced by batteries of fewer but of larger cells after the electrodes have been first brought in contact and afterwards separated from one another.

By gradually introducing greater resistances, like those furnished by the cadmium iodide solutions, the character of the discharge can be entirely altered as in rarefied gases. The arc-discharge changes first of all into the continuous glow-discharge. The difference in temperature of the two electrodes is in this case exceedingly great. If the resistance introduced be less than 50,000 Siemens units, and the electrodes are formed of platinum wires 2 mm. thick, the blue glow-light, which at this density of the air scarcely covers

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* Phil. Trans. clxix. p. 55 (1878).

¼ sq. mm., raises the negative wire to a most intense white heat, fuses the end to a large globule and keeps it fluid, whereas the end of the positive wire is only at a strong red heat. This extremely high temperature of the layer of gas surrounding the kathode contrasts very strikingly with the imperceptible heating which the same current causes in the thin metal wires conducting it. All metals behave like platinum. This glow-discharge, in which the negative pole glows much more strongly, is also obtainable with carbon electrodes by introducing suitable resistances. The same inversion in the strength of the glow can also be induced between mercury electrodes. If no resistance be introduced, the arc-discharge is obtained with white hot mercury vapour as a conducting medium and with the positive end glowing more brightly. With a resistance of 50,000 Siemens units, however, there is a small spot of hot glow-light on the surface of the mercury at the negative end, which causes brilliant volatilization and a white-hot glow of vapour, whereas the positive light only heats the surface slightly. The temperatures naturally become gradually smaller on increasing the resistance, but there is always a great difference between the negative and the positive electrodes. The resistance can easily be so regulated that only the negative wire glows and the positive is almost cold. On further increasing the resistance, the glow-discharge becomes discontinuous and a strong smell of ozone is perceptible. If, finally, the resistance is more than 9,000,000 Siemens units, there is no longer any trace of blue glow-light in the discharge. Extremely attenuated straight sparks following one another very quickly then appear, if the knobs of the micrometer are 1 mm. apart ; they have in all respects the same appearance as those produced by my influence-machine, without the Leyden jars, between the same electrodes. The sparks from both sources terminate at the surface of the electrodes in bright points which show the colour of the light from the vapour of the adjacent metal. The reason why the Holtz machine only gives thin sparks and no trace of blue glow-light is merely due, as we have seen above, to the poverty of the supply.

If the electrodes from 1600 cells consist of thin metal wires, the extremities when placed opposite to one another, even at a distance of 15 to 18 mm., appear covered with a very faint light which is only seen in total darkness. It is immaterial in this case whether a large resistance is introduced or not. The difference between the poles is distinctly noticeable under the microscope. At the extremity of the kathode, namely, there is a spot of blue glow-light towards which, separated by a narrow dark layer, the point of a small brush is directed. At the anode there is only a similar small brush, the point of which is in direct contact with it, and not separated by any dark space. If this point of light be increased by decreasing the distance, a strong smell of ozone is perceived. The metallic vapours which form the extremities of fine sparks are entirely wanting in this phosphorescent point of light. They only appear when the ends of the fine wires are brought within distances of less than 3 mm., after introducing the large resistances above mentioned. The thin straight sparks then fill up the whole length of the intermediate space. The luminous point is always discontinuous and accompanied by currents of air. If a point is taken as one electrode and a larger surface as the other, as for instance the knob of a micrometer, then only the former becomes luminous and with a light corresponding to its electricity. The surface of the knob remains dark. The particles of air electrified by the point migrate to the knob, and are there discharged without evolution of light. All these discontinuous discharges only cause very slight deflections in the galvanometer. By introducing all my cadmium iodide solutions scarcely any change is caused in the deflection of the galvanometer, so great is the resistance in the migratory discharge.

The brush-light can also be obtained with 800 cells, but naturally fainter and at smaller distances. The positive brush-light is formed by much smaller electromotive forces as soon as the resistance has been removed from the kathode. This is possible by using a flame, as already mentioned in my second communication. For this purpose a loop of thin platinum wire, as employed in spectrum analysis, containing a potassium salt, is placed in the faintly luminous Bunsen flame and used as the kathode. I now use as the most suitable salt potassium tungstate, which is obtained by adding tungstic acid to a solution of potassium carbonate heated in a metallic dish, as long as there is any evolution of gas. The clear solution is evaporated and the salt fused in a platinum crucible. It must be kept in a stoppered bottle, as it is very hygroscopic. A small bead of this salt remains a long time in the above flame, as the volatilization is slow and equal for both constituents. As the bead is hotter it decreases the resistance at the kathode to a somewhat greater extent than the more volatile and, therefore, colder bead of potassium carbonate which I have previously employed. In these experiments with the flame it is advisable to introduce a larger resistance into the circuit, in order to prevent the formation of the arc-discharge and consequent fusion of the wires on decreasing the distance between the electrodes. With this arrangement and in a dark room a thin positive brush is observed at 1 to 2 mm. from the edge of the flame, when the number of cells only amounts to one hundred. The distance increases with the number of cells. The current is always discontinuous, and only causes small deflections in the galvanometer. If the poles are interchanged, the light and current cease so long as the number of cells is less than 600–800.

That a transmission of particles of air accompanies the brush-light, caused by the immersion-battery, is best of all demonstrated by means of a vane which is caused to rotate rapidly by the reaction. The vane I used was simply made of aluminum wire, of which the pointed ends were bent in a horizontal direction at a right angle, in the well-known manner, and was supported at the centre, which was slightly hollowed out, on the point of a needle. The latter was attached to the metal tube in the middle of the plate of the mercury-pump, and was covered with a glass bell-jar provided with a lateral tubulure. Round the inner surface of the latter and at the height of the tubulure and the vane is a strip of metal, which is connected to one pole of the battery by means of a wire passing through a cork in the tubulure. The vane forms the other electrode. It was thus possible to observe its behaviour at the ordinary pressure as well as at any required degree of rarefaction. The distance between the extremities of the vane and the strip of metal must be adjusted to the density of the gas, in order that the brush-light may appear with the electromotive force which is employed. I therefore used two tubulated glass bell-jars of different diameters (9 and 18 cm.), and altered the length of the vane when necessary.

The details mentioned in our text-books as to the behaviour of the vane in rarefied air are scanty and incorrect. It is usually stated that the vane no longer moves because the electricity never attains the necessary density at the point. At pressures of the air, however, greater than 40 mm., a rotation of the wheel can be brought about whether it be negative or positive. Both extremities then show a faint luminosity. With smaller pressures I did not succeed in causing the negative wheel to rotate with the methods given. On the other hand, I was able to obtain a rotation of the positive wheel at pressures ranging from this down to 9 mm. In order to confine the light at these greater pressures to the point, the rest of the surface was covered with a layer of varnish.

The rotation of the wheel can be prevented at any pressure by sufficiently increasing the strength of the current. In order that rotation may occur, the glow-discharge must not take place in the intermediate space, but must remain confined to the immediate neighbourhood of the point. At pressures under 70 mm. it was very easy, with the number of cells at my disposal, to cause and prevent the rotation at will, by suitably altering the resistance introduced into the circuit. With the smallest pressure of 9 mm. as above, and employing 1600 cells, the resistance of all my cadmium iodide solutions was far from sufficient to allow of rotation in the 18 cm. bell-jar, with a space of 7 cm. between the ends of the vane and the strip of metal. Rotation only took place after a column of pure amyl alcohol, 10 cm. long and 11 mm. wide, had been introduced into the circuit. The discontinuous current was thereby weakened so much that it only deflected the galvanometer through 30 mm. when the latter was shunted by 100 Siemens units. There can be no doubt but that it would be possible to obtain the rotation of the positive wheel at still greater rarefactions by employing a wider bell-jar. On the other hand, this does not appear to be possible when the wheel is negative. In this case, as already mentioned, the rotation ceases at 40 mm. pressure, however large a resistance is introduced.

This difference is a consequence of the facility with which the so-called positive part of the glow-discharge is formed in rarefied gases. When the negative wheel is at rest it is observed in a dark room that generally only one of its points is covered with blue glow-light. Faint positive light always appears at the nearest point on the strip of metal, and often also in the immediate intervening space. On reversing the current, the wheel, which has become positive, rotates, and generally only its two extremities are luminous. Negative glow-light does not appear at the opposite parts of the strip of metal, nor is positive light to be detected in the intervening space. Only a compact brush of positive light shoots through the space to the strip of metal at shorter or longer intervals. When the positive wheel no longer rotates, the negative glow-light is always recognizable on the metallic strip ; in that case also only one of its points is luminous. The faint discontinuous current appears with the brush-light at a higher pressure of the air with a sufficient number of cells when the vane is the kathode than when it is the anode. In order to obtain it in the latter case, the density of the gas must be lowered, since the distance from the metal strip remains constant. The discontinuous current, too, which occurs when the vane is negative, always deflects the galvanometer, and often much more strongly than is the case under the same conditions (*i. e.* at the same density of the air, with the same distance of the electrodes and the same number of the cells) on reversing the poles. Thus, with a pressure of 120 mm. and a space of 25 mm., the negative vane rotated by 1600 cells caused a deflection in the galvanometer, shunted by 100 Siemens units, of 125 mm., which was only 17 mm. in the case of a positive vane.

It is not absolutely necessary that the vane should terminate in points in order to obtain a rotation with the galvanic battery in rarefied gases. By employing two small disks of aluminum 3 mm. in diameter, attached laterally, at the extremities, and varnishing the whole of the wheel with the exception of the two opposite surfaces of the disks, it rotated under the conditions described above when positive and when the pressure of the air was not less than 20 mm. Both the free surfaces shone with a reddish-yellow light, everything else remaining obscure.

If this wheel with the disks is negative at lower pressures than 3 mm., then, as I mentioned in my first communication, both surfaces are covered with blue glow-light which gradually extends, on increasing the rarefaction, in a straight line into the surrounding space. These glow-rays do not directly cause any rotation. Mr. Crookes has recently repeated a large number of the facts, regarding the negative glow-light, which I have described in my first communication and has brought them before the Royal Society in London and the French Academy* without referring to my investigations. He used his radiometer as a fly-wheel, by fitting it up with aluminum plates, covered with mica on alternate sides. At a high rarefaction all the free surfaces are covered with glow-light, which spreads out to a considerable distance. The mill only rotated when these hot glow-rays reached the glass side of the vessel and heated the places touched. It is the thermal radiation of the glass side therefore which first causes a rotation.

In addition to the fly-wheel I have also used a light movable windmill for the above purpose. As in Mr. Crookes' radiometer, a glass cap supported four glass rods fused on to it with mica disks, which were inclined at 45° to the horizon and supported on the point of a short needle. This windmill stood insulated on the brass plate of the air-pump in a glass bell-jar which terminated at the top in a tubulure. A pointed wire was passed through the latter into the bell-jar and formed one electrode, the plate being the other. The current of air from the point impinged on the mica disks and caused the mill to rotate. It remained stationary when the whole bell-jar was filled with the glow-discharge.

Reviewing all the facts in this paragraph, and having regard to the delicacy of fly-wheels and vanes, there is no doubt that in the glow-discharge there is no propagation of gas particles; and that, therefore, when it takes place, the transmission of the current everywhere, including the dark layers of the positive light and the dark space, is due to another cause. Faraday also held this view, and alluded to it in § 1551.

I cannot, therefore, assent to a theory which Prof. G. Wiedemann has proposed in his two papers. Prof. Wiedemann only used the current of a Holtz machine, as he assumed that he had in this case the simplest, and therefore the best conditions for his investigation. He considers the current as continuous when the combs are connected by metallic conductors. This supposition, however, is just as incorrect for this current as for that from a frictional machine. The circuit in both currents always contains layers of air between the combs and the rotating disk. With the help of the rotating mirror, the brush-light here is found to be just as discontinuous as under the conditions above mentioned.

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* Phil. Mag. [5] vii. p. 57 (1879).

Prof. Wiedemann has demonstrated similar relations to those alluded to in the case of the fly-wheel, by using the induction-current. By the ingenious use of a heliometer lens he determined the time which elapses between two discharges in a rarefied gas, and that which the inadequate source of electricity required to reproduce the charge which had disappeared. If only one comb of the Holtz machine was in direct metallic communication with the one spherical electrode in the gaseous space, and the other comb and the second similar electrode were connected to earth, then the discharge in the rarefied gas, the pressure remaining the same, took place at shorter intervals when the kathode communicated with the comb than in the opposite case. I consider it probable that this difference is caused by the transmission-process which takes place between the points of the comb and the rotating glass plate in air of ordinary density. I cannot assign the same importance to this fact that Prof. G. Wiedemann does, who explains by it the large extension which the positive light in tubes generally has in comparison with that of the negative glow-light. If there were any such relation, the extension of the negative glow-light would depend upon the distance between the electrodes. This, however, does not affect it at all and, as I have already shown in my first communication, it depends solely on the surface of the kathode, the density of the gas, and the strength of the current.

§8. Faraday's theory of induction accounts easily, in general, for the influence which distance between the electrodes and density of the gaseous dielectric exert on its electrical behaviour. I again quote his statement of these relations literally.

"There is perhaps no distance so great that induction cannot take place through it; but with the same constraining force it takes place the more easily, according as the extent of dielectric through which it is exerted is lessened." (1303.)

"1375. *Rarefaction* of the air does not alter the *intensity* of inductive action; nor is there any reason, as far as I can perceive, why it should. If the quantity of electricity and the distance remain the same, and the air be rarefied one half, then, though one half of the particles of the dielectric are removed, the other half assume a double degree of tension in their polarity, and therefore the inductive forces are balanced, and the result remains unaltered as long as the induction and insulation are sustained. But the case of *discharge* is very different; for as there are only half the number of dielectric particles in the rarefied atmosphere, so these are brought up to the discharging-intensity by half the former quantity of electricity; discharge, therefore, ensues, and such a consequence of the theory is in perfect accordance with Mr. Harris's results."

"1364. First as to the *distance* between the two balls used, or in other words, the *thickness* of the dielectric across which the induction was sustained. The quantity of electricity, measured by a unit jar, or otherwise on the same principle with the unit jar, in the charged or inductive ball, necessary to produce spark discharge, was found to vary exactly with the distance between the balls, or between the discharging points, and that under very varied and exact forms of experiment."

"1365. Then with respect to variation in the *pressure* or *density* of the air. The quantities of electricity required to produce discharge across a *constant* interval varied exactly with variations of the density . . . . ."

The results of Harris's experimental research quoted by Faraday in the last two paragraphs cannot be considered as absolutely correct laws. They are the further removed from reality the smaller the density of the gas.

Harris[*] concluded from his second law that an insulated conductor could not retain the feeblest electrical charge in sufficiently rarefied air. Matteucci[†] also held this view, and it is self-evident according to the prevalent theory, which ascribes the retention of the electrical fluid on the surface of the conductor to the pressure of the air.

Experiments, however, made at the end of the last century demonstrated, in contradiction to this conclusion, that considerable electrical tensions could exist in the vacuum of a barometer which had been carefully boiled. They induced Riess, in his work on Frictional Electricity[‡], "to consider it as probable that an electrified body would always retain its electricity in a space entirely free from air."

By passing pure carbonic acid through glass tubes with projecting wires and, after sealing them up, absorbing the gas with caustic potash, Gassiot obtained a degree of rarefaction through which a small induction-coil would no longer discharge itself.

Similar vacuum-tubes can be produced more easily, and with a still more remarkable result, by means of Geissler's mercury-pump. In my first communication I showed that, with degrees of rarefaction obtained with it in cylindrical tubes of 1 to 2 cm. diameter, where the wire electrodes are in the axis, that, however small the distance between them, they refuse to discharge electrical tensions which in ordinary air give sparks 16 cm. long. Tubes of this description have, through Geissler and Alvergniat, become very general. In constructing them it is necessary to make sure that the wires have previously been deprived as completely as possible of their occluded gases.

These tubes are generally adduced only as proofs of Faraday's theory that a vacuum is a non-conductor. I have, however, shown, so far as it was possible with the induction-current, that their behaviour is chiefly due to the large resistance which is formed in the neighbourhood of the kathode at low tensions of the gas. At the end of my second communication I pointed out that at these high rarefactions the formation of the current is again possible with a very small number of cells as soon as that obstacle at the kathode has been removed. We shall subsequently find this supposition verified after we have understood the nature of the glow-light.

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[*] Phil. Trans. p. 243 (1834).

[†] *Ann. de Chim. et Phys.* [3] xxviii. p. 385 (1850).

[‡] Vol. i. p. 40.

So long, however, as that hindrance exists at the kathode, the electromotive force, which the glow-discharge requires for a constant distance between the electrodes, has a minimum value for a certain density of the gas, and again increases on further increasing the rarefaction. It was of interest to know this minimum value for subsequent reference. I determined, therefore, the rarefaction at which the smallest number of my cells still discharged themselves in a cylindrical tube 4 cm. in diameter with wire electrodes at a distance of 1 cm. fastened in its axis. This was essentially the same for air and for hydrogen, and corresponded to a density of 0·5 to 0·75 mm. The number of cells which still causes a glow-discharge is somewhat, but not much, smaller with hydrogen than with air. It also depends somewhat on the nature and thickness of the electrodes. The following numbers were obtained in the case of hydrogen :—

If iron or platinum wire 1·5 mm. in thickness were used, then 180 cells were required to cause a discharge at the most favourable rarefaction. By employing the device of J. Herschel, and allowing the sparks from the Leyden jar of a Holtz machine to pass simultaneously at the above distance, it was possible to obtain a constant glow-discharge with 148 cells. Aluminum wires under these conditions, with the assistance of the sparks, even transmitted a constant current from the smallest number, 136 cells. Gas-coke was the most unsatisfactory material for the electrodes, as 220 cells were necessary with the assistance of the sparks before a constant glow-discharge was obtained. A sufficient resistance was in this case introduced into the circuit in order to prevent the arc-discharge which is so easily formed with carbon electrodes.

It is not possible to cause the discharge of a smaller number of cells by decreasing the distance below 1 cm. How small an influence is exerted at these small pressures of gas by the length of the path occupied by positive light on the amount of electromotive force necessary for the glow-discharge, was shown by using a longer tube of the same diameter containing hydrogen at the same pressure and platinum wires 16 cm. apart. The constant glow-current was produced by 200 cells at this long distance with the help of the spark.

From the phosphorescent character of the light already established, emitted by the molecules of gas which caused the so-called positive discharge, it is evident that the latter are, according to Faraday, in a state of strain, since their thermal condition does not account for it. Notwithstanding the low temperature, it follows also from the changes which take place in the constitution of the molecules of chemically compound gases during the passage of the current. Berthelot has been largely engaged in investigating these actions of the electrical discharge, which he calls the *effluve electrique*, and uses the induction-current. The galvanic battery with its continuous current is no doubt much more suitable for their exact investigation. Up to the present, however, I have had no time to investigate these chemical actions in detail, and I have only casually made some experimental observations. Thus the compounds NH_3, N_2O, which, under ordinary conditions, require a strong red heat for their decomposition, are split up into their components when in the state of strain even at those low temperatures.

By means of the immersion-battery a third change, which is shown by all gases in the state of strain, can easily be demonstrated. The molecules in that case conduct not only in the direction of the glow-current, but also perpendicular to it, and therefore in every direction. To demonstrate this fact I made use of a glass tube, as represented in fig. 11, Pl. III. Two thin platinum wires cemented into capillary tubes were placed at right angles to the direction of the current, so that the ends inside projected 2 to 3 mm. and were 2 mm. apart. When the whole section of the rarefied gas in the tube 8 mm. wide was made luminous with positive light, by passing a current through it from 1000 cells and introducing a suitable resistance, it was possible, by means of the thin platinum wires, to demonstrate the conduction of the gas for a few galvanic cells in the intervening space which, without a current, is an insulator. It must be remembered in this simple experiment that the two platinum wires, which are not infinitely thin, always deflect a small part of the principal current through the circuit in which they are, and in which there is a second galvanometer. This branch current is easily rendered harmless for our purpose by passing the current from the galvanic cells in quick succession first in one direction and then in the other, and observing the deflections in the second galvanometer. The arithmetic mean of these corresponds to the intensity of the current conducted by those few cells and by the molecules of gas in a state of strain. It was proportional to the number of cells, when less than 100, if the principal current remained constant. The deflection caused by the same number of cells increased with the strength of the principal current, thus showing that the conducting power of the gas had increased, as we shall demonstrate more clearly in the next paragraph.

By means of the two platinum wires, it can also be proved that the nonluminous molecules of gas which form the dark layers of the positive light and the dark space are capable of conducting a current. If both wires are in the dark space, then the deflection caused by the same number of cells for the same strength of the principal current in the tube (Pl. III. fig. 11) is smaller, since in this case a smaller density of current is formed, owing to the shape of the kathode employed.

The stratification of the positive light appears less enigmatical when it is recognized as a phosphorescent light. When we remember that the luminosity of our phosphorescents depends on exceedingly minute causes as yet uncontrollable by experiment, then the fact that equal sections of the gas are partly luminous and partly not, cannot appear so very strange to us as formerly, when we assumed that luminosity was caused by a high temperature. I do not in any way wish to detract from the interest of the above fact. On the contrary, I am of opinion that whoever gives the correct explanation of the stratification, capable of experimental proof, will have adduced a most important fact as regards phosphorescence. During the course of my work I have collected a number of observations on stratification, but I do not wish to deduce as yet any general principles from them. After closing the circuit of the immersion-battery, the positive light is very frequently uniformly luminous without dark strata, with the exception of the dark space in front of the negative glow-light, which is always present. Sometimes a single narrow dark layer is also present from the commencement at that end of the positive light which borders on the dark space. Then several new ones are gradually formed there, and suddenly the whole column is divided in a most beautiful manner into light and dark strata. Sometimes the dark, and sometimes the light strata are wider. The surface of the anode always appears luminous even when the rest of the intervening space up to the negative glow-light remains dark. The strata remain unchanged if it is possible to keep the strength of the current unaltered. The changes which so frequently take place in the former are always simultaneous with alterations in the strength of the current. When the number of strata increases, the new strata are generally seen to be formed at the surface of the anode; they detach themselves from the latter and join the others, which they push forward. The anode is, however, at no instant deprived of positive light. If, conversely, the number of strata decreases, the latter then retreat towards the anode and merge singly into the stratum of light which always surrounds it.

The luminous strata are bounded by bent surfaces, of which the convex side is generally turned to the kathode. This, however, is not always the case; the reverse also occurs according to the shape of the inner surface of the glass side. With a glass sphere, to which a cylindrical tube (Pl. III. fig. 12) was fused, containing hydrogen at a pressure of 4 mm., a current which caused a deflection of 30 mm. in the galvanometer, when shunted by 2 × 50 cm. of the rheostat, gave, when traversing the gas from *a* to *c*, only a single bright layer at the spot where the sphere bordered on the cylinder. This layer was convex towards the anode. The rest of the space, with the exception of the glow-light about the kathode and of the positive light on the anode, was dark. The latter, as ordinarily, was convex towards the kathode. At a high rarefaction there was in the sphere of this vessel, just after closing the current, a faint luminous mist together with the luminous stratum at the entrance to the cylindrical tube, and this, after a few moments, became transformed into a second luminous stratum which pushed the first into the cylindrical tube and took its place. In this case the new stratum was distinctly not formed at the anode as in cylindrical tubes. I have often obtained a single similar luminous stratum in cylindrical tubes at points where a solid object projected and somewhat contracted the section of the gas.

Münster, May 14, 1879.

PHYSICAL MEMOIRS.

RADIANT ELECTRODE MATTER

AND THE SO-CALLED

FOURTH STATE.

BY

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Preface.

THE interest aroused by my vacuum apparatus, when exhibited in the Paris International Electrical Exhibition of 1881, not only in my colleagues, but also in lovers of natural science, seemed to show that the publication of a comprehensive account of the investigations thereon would be acceptable; it has been published in four papers in the Memoirs of the Imperial Academy of Vienna. In the present complete edition many parts have been abridged and others extended and corrected in the light of the results of later investigations. A communication is added as appendix:—"Contribution to the explanation of Zöllner's Radiometer," whose simple phenomena of motion may assist in the easier comprehension of the, for the most part complicated, motions of electrical radiometers.

All the vacuum apparatus described here I have constructed in the physical laboratory of the Vienna University, and some is now in the Conservatoire National des Arts et Métiers, in Paris. The firm of Messrs. F. O. R. Goetze, of Leipsic, have undertaken the construction of the apparatus, and I gladly take this opportunity of testifying that the samples sent me have been constructed with great skill and knowledge of the subject.

Is there a Fourth State of Aggregation of Matter?

> Causas rerum naturalium non plures admitti debere, quam quae et verae sint et earum phaenomenis explicandis sufficiant (*Princ.* I. iii.).—NEWTON.

AMONG physicists the view has for long been held that investigations on electrical discharges in rarefied gases will lead to a knowledge of the nature of electricity. To this circumstance we owe a copious literature, of which I will here only mention the beautiful investigations of W. Hittorf*, which he published in the year 1869, in two papers entitled "On the Conduction of Electricity in Gases," and which have been taken little account of even by colleagues, perhaps because the title was somewhat too modest.

Mr. William Crookes, to whom Hittorf's work was apparently unknown, gave in a lecture† to the British Association in Sheffield, on August 22nd, 1879, a review of the results obtained by him, which do not differ substantially from Hittorf's, and are only to be distinguished by a more elegant form of experiment. The conclusions, however, to which these experiments led Mr. Crookes are new, and they aroused general attention and no small interest, especially in those circles which delight in occupying themselves with questions of transcendental views of the universe.

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* Poggendorff's *Annalen*, vol. cxxxvi. [*vid. supr.* p. 111].

† This lecture was published in German, entitled "Radiant Matter or the Fourth State. By William Crookes. Translated into German, with the author's sanction, by Dr. Heinrich Gretschel," Leipsic, 1879. The following papers appeared also :—"On the Illumination of Lines of Molecular Pressure and the Trajectory of Molecules," Proc. R. S. vol. xxviii. no. 191; Phil. Mag. 1879, ser. 5, vol. vii. p. 57; 'Nature,' 1879, July 3 and 10.

To explain the phenomena observed in the exhausted spaces, Mr. Crookes assumes that the very rarefied residual gas exists in a new "ultragaseous" state, which he calls the "fourth state," and designates by an expression borrowed from Faraday, "radiant matter."

The assumption of the fourth state is justified by Mr. Crookes in the following manner * :—

"The further this process (the rarefaction) is carried the longer becomes the average distance a molecule can travel before entering into collision ; or, in other words, the longer its mean free path the more the physical properties of the gas or air are modified. Thus, at a certain point, the phenomena of the radiometer become possible, and on pushing the rarefaction still further, *i. e.* decreasing the number of molecules in a given space and lengthening their mean free path, the experimental results are obtainable to which I am now about to call your attention. So distinct are these phenomena from anything which occurs in air or gas at the ordinary tension, that we are led to assume that we are here brought face to face with matter in a fourth state or condition, a condition as far removed from the state of gas as a gas is from a liquid."

There are, accordingly, two reasons which point to the need of the assumption of a fourth state :—1. The high degree of rarefaction. 2. The difference of the phenomena from those which take place under ordinary pressure.

We will submit these reasons to a discussion in order to ascertain what probability is to be assigned to the hypothesis assumed.

The three states of aggregation of bodies hitherto known depend upon the difference in the mobility of their smallest particles as well as on the different conditions of cohesion. In the gaseous state the particles attain the highest degree of mobility and the cohesion is infinitely small. What now characterizes this hypothetical fourth state? Is it perhaps a still greater mobility of the particles and a still smaller degree of cohesion? This is scarcely admissible so long as molecules and atoms exist as such. This question, too, is not left unanswered in the publication in question. It is there said * :—"In studying this fourth state of matter we seem at length to have within our grasp and obedient to our control the little indivisible particles which with good warrant are supposed to constitute the physical basis of the universe. We have seen that in some of its properties radiant matter is as material as this table, whilst in other properties it almost assumes the character of radiant energy. We have actually touched the borderland where matter and force seem to merge into one another, the shadowy realm between known and unknown, which for me has had always peculiar temptations. I venture to think that the greatest scientific problems of the future will find their solution in this borderland and even beyond; here, it seems to me, lie ultimate realities."

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* 'Nature,' 1879, p. 419.

Radiant matter would thus consist of very small indivisible particles, the ultimate atoms, into which the residual gas and any ponderable matter resolves itself at the highest degree of rarefaction, which is stated to be at a millionth of an atmosphere.

Ponderable bodies can be decomposed by forces we are acquainted with into simpler substances known as elements. The chemist Prout, and after him the celebrated Dumas have established the fact that a certain regularity exists between the atomic weights of simple substances according to which all simple bodies have an atomic weight, which is equal to a multiple of the atomic weight of a still unknown body whose equivalent is only half the equivalent of hydrogen. Moreover Dumas, guided by the analogy of the compounds which are formed by organic radicals, came to the conclusion that the equivalents of simple substances which belong to one and the same natural family form an arithmetical series in the same way as the radicals of organic chemistry. These facts point with great probability to the assumption that the bodies which we regard as simple substances are compounds of a higher order, that they are very complicated aggregates of other elements which themselves are compounded, but that finally they can all be decomposed into one single matter. The decomposibility and invariability of chemical elements has especially in recent times been assumed and established

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* 'Nature,' 1879, p. 439.

in various ways by investigators, such as Mendeleeff, Lothar Meyer, Norman Lockyer, Gorup Besanez, Fr. Wächter, and others.

The assumption of the unity of matter, which from a philosophical point of view is self-evident, finds support also in comparative spectrum analysis. Cimician's investigations in this direction show that on the basis of Mendeleeff's series and the *homology* of spectra it would be possible to reduce all the elements of the chemistry of to-day to the typical elements hydrogen, lithium, beryllium, boron, carbon, nitrogen, oxygen, and fluorine. All other elements are formed from those mentioned, by the addition of oxygen in different forms of condensation. But some of these typical elements too, carbon, boron, and beryllium, as well as magnesium, possess homologous spectra, and must therefore be compound bodies. Whether the rest of the elements—hydrogen, lithium, nitrogen, oxygen, and fluorine—are to be considered as the ultimate constituents can scarcely, according to Cimician's views, be determined by spectroscopic means.

Matter is accordingly capable of a further divisibility, and it is possible that in its ultimate division it would give that so-called imponderable matter which we call æther and which reveals its existence by the mode of motion of radiation, and whose material character and inertia is proved in that it exchanges its motion with ponderable matter.

We will now consider the methods which we can employ to decompose bodies. These are reducible to the molecular work which heat, electricity, and chemical force can perform. Very complicated molecules like those of organic substances can be decomposed even at moderate temperatures; on the other hand simple substances, even when exposed to temperatures above 1500° C., remain undecomposed. Like the energy of heat, so also the energy of the strongest electrical currents and that of chemical affinity have proved too weak to resolve the bond of the ultimate atoms into the atoms of the elements. If we had those smallest particles which form the "physical basis of the universe," they must certainly be of quite a different nature to our elements, so that the name "state" would not even be applicable, they might possibly be identical with the particles of æther. This, however, is not the case, since the molecules of radiant matter preserve their *characteristic chemical* properties, as Mr. Crookes himself has experimentally shown. Moreover, that the observed phenomena of phosphorescence, of shadow, of magnetic deflection, and also the phenomena of motion commence in different gases at different pressures is in accordance with the conclusions which follow from the kinetic theory of gases, and show that in rarefied gases we have still to do with *actual* molecules ; the metallic deposit in the region of the negative electrode also favours this view.

Experiments, too, with the plate of quartz, which will be more minutely described afterwards, have shown that we have here not to do with the radiation of æther matter but with the movement of gaseous particles (p. 250, *postea*).

Mr. Crookes believes he has attained the ultimate division of matter by means of a high degree of rarefaction, stated to be at a pressure of a millionth of an atmosphere, 0·00076 mm. Mr. Crookes, when he was led to this assumption, may perhaps have had present to him the idea that a liquid body passes more easily into the gaseous state the smaller the cohesion which keeps the particles together and the less the external pressure which acts on the particles, and that also dissociation of complicated molecules takes place much more easily at a reduced pressure. It must, however, on the other hand, be mentioned that that part of the energy of molecular motion which overcomes the pressure is relatively small compared with that part which in evaporation must overcome cohesion, and in dissociation chemical affinity, but which is certainly infinitely small compared with that part which is necessary to tear asunder the bonds of the primitive atoms.

Moreover, no such high degree of rarefaction is necessary for the phenomena of radiant matter as Mr. Crookes has obtained, for direct manometer measurements showed that even under a pressure of 0·01 mm. of mercury a current of moderate intensity (with a spark 2 cm. long) no longer passes through the tube. I am firmly convinced that even with a rarefaction of a trillionth, from the computation of the kinetic theory of gases, we should still have about 21 *molecules* in a cubic centimetre of air, and that a decomposition of the same into the ultimate atoms is not to be expected until another, more powerful source of energy has been discovered than the ones known up to the present time.

If the supposition were correct that gaseous matter can be converted by rarefaction into the fourth state, then the heavenly bodies which hover in a better vacuum than we can ever obtain must resolve themselves by degrees into ultimate matter.

Still less can I recognize the necessity for a new state because these phenomena are "different" from everything which has been observed at ordinary pressures. The necessity of any new supposition would only then be proved if the phenomena could not be explained by what we know at present.

On these grounds I cannot decide to adhere to the existence of the fourth state, and incline just as little to the view that we are here touching the borderland "where matter and force seem to merge into one another;" but least of all that we have here an open door into the world of four dimensions, as many transcendental thinkers find credible.

How matter and force can merge into each other is a secret which Mr. Crookes has omitted to explain.

The Dark Space in the Glow-light.

In an ordinary Geissler's tube filled with air at a pressure of about 0·5 mm. a red brush of light is seen at the positive pole, which, consisting of light and dark strata, fills the greater part of the tube—at the negative pole a blue light, the so-called glow-light, and between the two a dark space, to the explanation of which I shall subsequently refer. On continuing the rarefaction the strata of positive light disappear gradually, and the glow-light, which is always separated from it by the dark space, spreads over the whole length of the tube. On more carefully examining the glow-light a second relatively dark space can be quite clearly distinguished at the electrode, which is sharply defined from the first by a broad band of glow-light of decreasing intensity. The electrode itself is very often covered with a yellow, dust-like layer. which has the appearance of gold dust, and is a phenomenon of phosphorescence of the furthest layer of oxide.

This dark space, which has long been known and which is very accurately described by Prof. Hittorf, Mr. Crookes considers to be the "mean free path of the gaseous residue." The reasoning for this supposition may follow here and speak for itself.

"This* dark space is found to increase and diminish as the vacuum is varied, in the same way that the mean free path of the molecules lengthens and contracts. As the one is perceived by the mind's eye to get greater, so the other is seen by the bodily eye to increase in size; and if the vacuum is insufficient to permit much play of the molecules before they enter into collision the passage of electricity shows that the 'dark space' has shrunk to small dimensions. We naturally infer that the dark space is the mean free path of the molecules of the residual gas, an inference confirmed by experiment."

The reasoning of Mr. Crookes is therefore: A and B change in the same manner if C changes, therefore A must *equal* B. Reasoning in this way we could, for example, find that the pressure in a certain volume of gas is equal to the number of molecules present, because both decrease in the same way as the mean free path. The fallacy is too apparent, and it helps us little that Mr. Crookes, by means of induction-sparks "actually illuminates the lines of molecular pressure." The dark space is no mean free path, and only a phenomenon *dependent* on it, as we shall easily understand after we have recognized the nature of radiant matter.

It is sufficient to make a few experiments with electrodes of different metals—platinum, copper, silver, zinc—to obtain an insight into the processes in the dark space. By using an induced current, giving a spark of about 6 cm., the glass sides even in the course of half-an-hour are covered with a mirror of the corresponding metal. The metallic coating is strongest near the kathode, and extends as far as the glow-light.

If the tube near the negative pole is placed between the limbs of a horseshoe magnet the glow-light contracts near the electrode, and a smaller portion of the glass tube becomes coated with metal. By putting glass plates opposite plate-shaped platinum electrodes, I obtained in this way beautiful platinum mirrors.

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* Nature,' 1879, p. 419.

Aluminum is the only metal I know which gives no appreciable mirror on glass, and is therefore called "non-volatile." The slight deposit which the glass also shows on the use of this metal, and which can only be detected by the phenomena of phosphorescence, to be examined later, might arise from other metals from which the aluminum had not been completely purified.

I am inclined to look for an explanation of the reason that the aluminum particles do not stick to the glass either in their chemical constitution or in their properties of adhesion. But particles of aluminum also are torn off and transported, and move until there is an opportunity of sticking to a place on the positive or negative electrode. There can accordingly be no doubt that individual particles of the electrodes become mechanically detached by the electrical current, not by evaporation, and are shot out perpendicularly to the surface of the electrode, and with a relatively very great velocity. The particles are charged with statical negative electricity, and themselves moving away they transport the latter *convectively*, and in this way keep up the conduction between both electrodes. That particles of gas also partake in this electrical convection is a matter of course. By this stream of particles the gas is forced away from the electrodes just in the same manner as in a gas-flame the issuing gas forces the particles of air before it and forms the dark space close to the orifice into which very few molecules of oxygen can penetrate, and which is the greater the greater the velocity with which the gas issues. At the boundary where the particles of the electrodes clash with the molecules of gas, the former are diverted into all possible directions from their original rectilinear progressive motion by impacts of the latter in all directions. A mutual diffusion of particles of the electrodes and of gas takes place, accompanied by a deposition of the former on the glass walls. As the pressure must be equal in all parts of the tube their number in the unit of volume must be smaller, and therefore that space in which particles of the electrodes have not yet mixed with molecules of gas appears relatively dark. The agitation of the material molecules with their envelopes of æther at the boundary where the particles of the electrodes and gas meet will be violent, since one part of the progressive motion of radiant electrode matter becomes changed into atomic motion and motion of the envelopes of æther ; hence the phenomena of heat and phosphorescence must be gradually more intense there, and gradually decrease with the distance from the electrodes.

The particles thus move in straight lines through the dark space, and the boundary where they collide with the particles of gas and with one another is distinguished by its great brightness. Outside this bright boundary the particles of gas and of the electrodes move in all possible directions, and in proportion as the particles of gas preponderate in number the intensity of the *glow-light* decreases. I designate by this latter name the mixture of the particles of the electrodes and of gas which lies between the dark space on the electrode and the dark space next following.

As the particles of the electrodes and of gas of the glow-light must be at the same temperature, we must have

$$MU^2 = mu^2,$$

if M, U, m, u express the mass and velocity of a particle of the electrode and of gas respectively. Since it is very probable that the particles of the electrodes are of different sizes, often large lumps, M shall be taken to represent the mass of a particle of mean magnitude. We thus obtain for the velocity of a particle of the electrode

$$U = \sqrt{\frac{m}{M}}u,$$

a magnitude which will be smaller than the molecular velocity of the particles of gas, since in most cases M will be greater than m.

In the bright *bounding layer* of the dark space the number of particles of gas will be very small, and therefore, considering them as particles of the electrodes, we can assume that in the unit of volume there are N particles of the electrodes which move about in *all* directions. In the dark space there are N_0 particles in the unit of volume, which, however, move towards the bright layer *only* in *one* direction. Hence the pressure on the unit of surface of the bright layer of the glow-light which the progressive molecules of the dark space exert is

$$p = N_0 M U_0^2$$

where U_0 expresses the velocity of the progressive motion of the particles. On the other hand, the pressure from the opposite side of the bright layer is

$$p = \tfrac{1}{3} N M U^2,$$

where U, however, expresses the velocity with which the particles move in all possible directions.

Since the bright layer is in equilibrium we must have

$$N_0 M U_0^2 = \tfrac{1}{3} N M U^2;$$

and because we assume equality of temperature we also assume equality of the *vis viva* of a molecule, we find

$$N_0 = \tfrac{1}{3} N.$$

The number of molecules in the unit of volume of the dark space is one third that of the bright layer.

The smaller brightness of the relatively dark space depends chiefly on the smaller number of luminous particles of the electrodes, and not, as was assumed by Mr. Crookes, on the deficiency of impacts of the same with particles of gas.

If the particles of the electrodes strike against a fixed platinum plate, almost the whole energy of their progressive motion is converted into heat, and the platinum becomes red hot. On the other hand, in a collision between particles of the electrode and of gas the progressive motion of the former is simply transferred to the latter, and the movable particles cannot therefore be caused to glow. Their luminosity is caused by a discharge of electricity and not by collision, since the *emittent* kathode rays, as also the particles of the electrodes in the dark space in which they relatively infrequently collide, likewise phosphoresce.

As the entire mass of gas is in a stationary condition in the glass tube, the pressure in the dark space is not only equal to the pressure in the glow-light but is also equal to that at another point. We must therefore have

$$p = N_0 M U_0^2 = \tfrac{1}{3} n m u^2,$$

if n, m, u refer to gas.

Since the particles of gas move in all directions we shall now have, if the temperatures are equal, which is approximately the case,

$$N_0=\tfrac{1}{3}n \text{ and } U=\sqrt{\frac{m}{M}}u.$$

The velocity of the particles in the dark space is smaller than the molecular velocity of the gas, and can therefore, so long as the dark space remains visible, amount to several hundred metres.

At a higher degree of rarefaction the electrical tension necessary for discharge, as also the velocity of the particles thrown off, is greater, and as, moreover, the resistance of the residual gas is also less, the dark space increases more and more, and its limits disappear if the rarefaction reaches about 0·03 mm.

Even if the velocity of the electrode particles at a higher rarefaction is somewhat greater than the molecular velocity of the gases, it will never reach the magnitude of 800,000 metres per second deduced by Goldstein under certain assumptions which are by no means justifiable.

Mr. Crookes maintains that the *residual* gas inside the dark space exists in the fourth state, and calls it "radiant matter."

In my opinion *the matter which fills the dark space consists of mechanically detached particles of the electrodes which are charged with statical negative electricity, and move progressively in a straight direction.*

In order that no doubt may prevail as to the nature of this matter I call it "radiant electrode matter" (strahlende Elektrodenmaterie), in distinction to the so-called "glow-light," which consists of a mixture of particles of the electrodes and of gas.

If we consider the electrode particles to be infinitely small spheres, which are detached from the surface of a large sphere, we can, according to Plana's* calculation, write 1·645 for the mean density of the statical electricity of the particles of the electrode, if that of the electrode be taken as unity.

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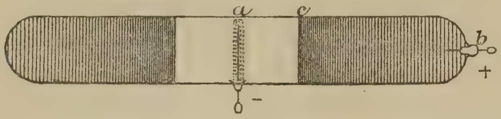
* *Mém. de l'Acad. de Turin*, 1845, 2 sér. vol. vii.

That the dark space is not identical with the mean free path of the rarefied gas is easily proved by calculation. For this purpose I carried out some experiments with air-tubes at a very small pressure. The pressure was measured by means of a manometer which I have described in an earlier paper "Ueber die innere Reibung der Dampfe"[*].

Fig. 1.



The following numbers are mean values of three series of experiments, p denoting the pressure and d the dark space ac in millimetres :—

p.	d.	pd.
1·46 mm.	2·5 mm.	3·650
0·66 "	4·5 "	2·970
0·51 "	5·8 "	2·958
0·30 "	7·8 "	2·348
0·24 "	9·5 "	2·280
0·16 "	14·0 "	2·240
0·12 "	15·5 "	1·860
0·09 "	19·5 "	1·755
0·06 "	22·0 "	1·320
0·02 "	?	?

At $p=0·09$ mm. the glass tube begins to phosphoresce; at $p=0·06$ mm. the phosphorescence is brisk; at $p=0·02$ mm., and with an induction-current giving a 2 cm. spark, it diminishes; at $p=0·01$ mm. it is very weak and only visible at the end of the tube. At a pressure estimated to be 0·005 mm. a faint flash through the tube is only to be seen from time to time in a perfectly dark room; if, however, at this degree of rarefaction the wire-shaped electrode be made the negative pole, phosphorescence is again apparent throughout the whole tube.

As the product pd shows, d is not inversely proportional to the pressure, which ought to be the case if it represent the mean free path.

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[*] *Sitzungsberichte der kais. Akademie der Wissenschaften*, 1878, vol. lxxviii.; *Repertorium*, vol. xv. p. 427.

If we assume further with Stefan the mean free path of the molecules of air at 760 mm. pressure to be 0·000071 mm., there results for the mean free path at $p=0·06$ to 0·09 mm., d about 22 mm.; and still more unfavourably at higher pressures, for example at $p=1·46$ to 0·04 mm., d about 2·5 mm.

The dark space is thus no mean free path of the molecules of gas, and only that mean distance from the electrode to which the detached particles attain in their straight paths before they burst into the crowd of opposing molecules of gas and are diverted in all possible directions by collision with the latter. Neither is it, however, the mean free path of the particles of the electrode; for we have no right to assume that the particles of the electrode in the dark space, like the molecules of gas in the dark part of a flame, do not collide with one another.

I will here further mention that I noticed the most beautiful phosphorescence at 0·04 mm., whereas Mr. Crookes states that he has seen the same at a 50 times smaller pressure, 0·00076 mm., at which in my experiments not even strong induction-currents can pass. As far I can learn from the accounts of radiant matter hitherto published, Mr. Crookes hoped to attain the high rarefaction by removing the last traces of any gas by a suitable absorbent. Experiment has, however, taught me that it is much easier to exhaust with a well-dried pump, for the absorbing bodies contain very many occluded gases which they evolve in a vacuum. Even metals contain gases in considerable quantities*, as is easily proved by exhausting a tube with platinum electrodes so far that with a weak current a beautiful phosphorescence of the glass tube is to be seen. If afterwards a stronger current is employed, so much gas is almost instantaneously liberated from the electrode that the phosphorescence completely disappears and the tube is filled with a whitish light. If the electrode is to be sufficiently freed from occluded gases, a strong induction-current must be passed through for hours without intermission, whilst the gases which are evolved are removed by continued exhaustion.

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* According to experiments by Dumas, 80 c. c. of aluminum heated in a vacuum to a temperature at which porcelain begins to melt, give off 15 c. c. of carbon dioxide and 88 c. c. of hydrogen measured at 17° and 755 mm.

Phosphorescence of Solid Bodies in Radiant Electrode Matter.

Radiant electrode matter causes in many bodies when struck by it spontaneous luminosity, a phenomenon known as *phosphorescence* and by many physicists as *fluorescence.*

The phenomenon of phosphorescence has long been known and minutely investigated by Prof. Hittorf and afterwards by Goldstein, Reitlinger, and v. Urbanitsky.

I may be allowed to cite literally here the description of this phenomenon as it appears in the second communication of Prof. Hittorf *:—

" The negative wire remains dark at the greatest rarefaction which the aspirator can produce without heating the gaseous medium ; only from the end opposite the anode does negative light issue, which, however, seems only to begin at some distance, because the mean dark layer [' dark space '] has acquired a considerable thickness. Its feebly luminous rays acquire a considerable extension, and pass through tubes a foot in length. The glass sides which bound it are fluorescent with a bright greenish-yellow light, and lose some transparence. Positive light cannot for the most part be seen. In such a cylindrical tube, therefore, the part which surrounds the positive wire and the space between the electrodes will be of a bright green, and that part at which the anode is introduced will be particularly bright, because it is opposite the end of the kathode."

" If the number of voltaic elements is increased, a green fluorescent light adds itself to that already described, as a more or less broad ring about the end of the kathode."

Whoever has once studied these matters will not doubt from the description given that Prof. Hittorf has noticed a phenomenon of so-called " radiant matter " which he designates simply " glow-light."

Mr. Crookes assumes that " radiant matter " is only present inside the dark space ; but, after we have seen that the glow-light too contains particles of the electrodes, we should be justified in assuming that in the glow-light also beyond the dark space phenomena of phosphorescence would make their appearance. In the course of my numerous experiments I have often observed that new glass tubes, even with a dark space of 10 mm., phosphoresce throughout their whole length, whilst in the interior the brush-light can be distinctly seen, especially if a circular plate of the diameter of the tube be taken as negative electrode.

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* Poggendorff's *Ann.* vol. cxxxvi. p. 198 [*vid. supr.* p. 137].

I will mention incidentally that at a high degree of rarefaction the discharges of the electric current take place also *through* the glass, and that not infrequently in capillary passages filled with rarefied air, what are called striæ (*Schlieren*), very bright whitely luminous lines of light of about 1 cm. in length, are to be observed.

Very beautiful bright sparks are also seen on the parts of the electrode which are covered with glass. The discharge passes through the glass into the wire of the electrode even when the latter has uncovered parts. The spark volatilizes the metal, and hence in the case of a copper electrode is bright red.

Carbonized paper raised to a white heat for a long time by means of radiant electrode matter shows, like the diamond, a bluish-green phosphorescence on using a weak induction-current. I have examined the carbon microscopically but found no diamonds, as I had suspected on account of the green phosphorescence.

If the negative electrode is a circular disc, it becomes covered with the glow-light over its whole surface. With an increased rarefaction the discharges contract more towards the edges, but there are still to be seen in the interior of the tube blue rays of electrode matter, even with a brilliant phosphorescence of the glass sides. At a pressure 0·03 mm. and with an induction-current giving 2 cm. sparks the discharges *only* take place at the edges of the disc and along the inner glass side, and the phosphorescent action of the rays has reached its maximum, whereby in the inner part of the tube no appearance of light is to be seen.

On this subject Mr. Crookes writes* :—“But at a very high exhaustion the phenomena noticed in ordinary vacuum tubes when the induction-spark passes through them—an appearance of cloudy luminosity and of stratifications—disappear entirely. *No cloud or fog whatever is seen in the body of the tube,* and with such a vacuum as I am working with in these experiments the only light observed is that from the phosphorescent surface of the glass."

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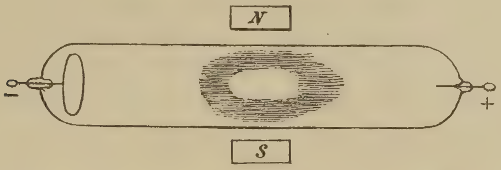
* ‘Nature,’ 1879, p. 421.

This circumstance may have led Mr. Crookes to the assumption that through the inner space of the tube in which no matter is apparent only "energy radiates," that here "matter and force appear to merge into one another."

The correctness of the above assertion, that the discharges *only* take place at the edges of the disc and are transmitted along the glass side is easily verified by bringing a horseshoe magnet near the side of the tube.

The light is attracted to one side and a section of the hollow cylinder of rays is seen with the glass side as an oval phosphorescence ring. The discharge along the glass side is much more strikingly shown by the electric lamp, the description of which will follow later.

Fig. 2.



The discharge at the inner glass side causes the outer surface of the glass tube to become very strongly positively electrical, and pendulums of thin glass bulbs of the size of a hazel nut are attracted from a distance of 1 to 2 cm. and adhere to the glass side.

If the electrode be attached to an elastic wire it trembles violently under the discharges, and the flickering phosphorescent light, which is accompanied by a chirping noise, presents a magnificent display. At the same time the electricity becomes stored up in the connecting wires, and discharges itself into the external air with the well-known noise, forming ozone.

The observation may, too, be of interest which I have made with many tubes at a pressure at which the phosphorescence of the glass has already appeared, whilst the inner part of the tube is still filled with thin blue clouds of radiant electrode matter. If the glass tube be put in conducting communication with the finger or a strip of tinfoil at the negative electrode on the side away from the positive pole, the blue clouds disappear and the tube shows a bright phosphorescence. Touching the piece of tube lying between the positive and negative electrodes has no action on this phenomenon.

In differently formed vessels this place of conduction may also be found between the positive and negative electrodes. If the tube at this place be strongly contracted, mere touching with the finger suffices to interrupt a current giving a 4 cm. spark. I have several times made this observation without having felt the ordinary physiological action of the induction-current. I shall refer later to this phenomenon.

The fact may also be mentioned that all bodies, for instance plates of mica, placed in the path of radiant matter become very strongly electrical, so that they adhere to wires or glass sides; hence in constructing all apparatus in which there are to be movable parts this circumstance must be borne in mind.

Mr. Crookes's explanation of phosphorescence is that radiant matter bombards the glass so that it begins to vibrate, and continues to give out light as long as the discharge continues (' Nature,' vol. xx. p. 420, 1879).

On the other hand Prof. Hittorf writes as follows about it:—"As I showed in my first communication, there are formed at the small cross section (of a wire surrounded with a tube up to the last section), if it is negative, very hot, slightly luminous *radiant particles of gas emitting light of a high refrangibility*, which extend straight through the whole tube to the opposite side and cause this to phosphoresce. . . . . If now the calcium sulphide be allowed to come into contact with the negative glow-light emanating from the cross section, the spots touched show an intense white luminosity which causes strong after-images in the eye when held near"*.

Radiant matter (glow-light) would therefore, also, according to the views of Prof. Hittorf, consist of particles of gas, and the latter, too, would have the property of emitting light of high refrangibility and cause phosphorescence.

Dr. Goldstein † is also of the same opinion as to the cause of phosphorescent light.

In order to test the correctness of this hypothesis a circular aluminum plate in which a section in the shape of a cross was covered by means of a plate of quartz 4 mm. in thickness was placed in the path of the rays. If the assumption mentioned were correct a phosphorescent cross on a dark ground must be formed on the glass side; for rays of higher refrangibility must pass through the quartz plate and cause phosphorescence on the side. This result, however, as was to be expected, was a negative one.

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* Wiedemann's *Ann.* vii. p. 586 [*vid. supr.* p. 207].

† *Wiener Berichte*, 1878.

In the following pages two pieces of apparatus are described which show some interesting phenomena of phosphorescence.

The plate of mica in the centre of the globe (fig. 3, p. 252) is about 4 cm. long and 3 cm. broad, and is coated with chalk on the side turned away from the saucer-shaped electrode. By using the plane electrode first as negative pole, the covering of chalk on the mica plate is directly struck by the rays and shines with a very bright orange-coloured phosphorescence. On breaking the current the feeble luminosity of the chalk still lasts for some time. If, however, the saucer-shaped electrode is afterwards made the negative pole, the coating of chalk shows first of all a very bright phosphorescent spot, forming after some seconds a ring of light which becomes continually larger. If after once breaking the current the *same* kathode is again used, no phosphorescent spot is formed; the phenomenon reappears, however, if after a few minutes the coating of chalk is first of all directly irradiated.

The explanation of this phenomenon presents no difficulty. The rays from the kathode which strike the bright side of the lamina only cause *indirectly* the phosphorescence of the layer of chalk by heating the lamina. The phosphorescence is excited afresh by heat, and as the latter spreads out in all directions in the plate of mica from the focus, continually larger circles will begin to be luminous. But this glowing, in consequence of the heating, only continues for a limited time, and the extinction begins therefore in the focus of the kathode-rays. The phosphorescent spot breaks up and forms a luminous ring which increases at its outer and decreases at its inner periphery, and in this way becomes larger and larger.

At a high degree of rarefaction and with a more powerful induction-current the plate of mica, when the phosphorescent ring is entirely extinguished, shows a small round and whitish spot, which is caused by a partial glowing of the mica lamina.

The experiment succeeds best of all when the mica lamina is *directly* irradiated by a single flash only, and after about 50 to 60 seconds is warmed from the back. The experiment may also be reversed. The mica lamina is warmed from the back first of all for about 3 to 4 seconds, and afterwards the layer of chalk is irradiated with a single flash. A dark circular disc is then seen on a bright phosphorescent ground, which is explained by the fact that the heated spot very quickly loses its phosphorescence.

This apparatus shows thus in an elegant form, not only the property of self-luminous bodies of being *caused to phosphoresce again by heating* if they have first of all been made self-luminous by direct radiation but remain dark on further heating, but also allows the velocity with which heat is transmitted in any plate to be demonstrated.

Fig. 3.

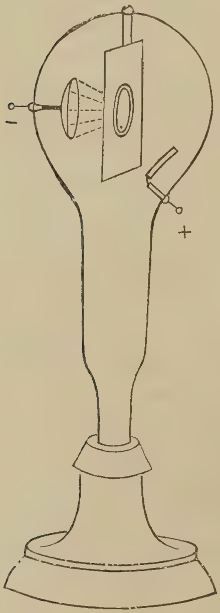
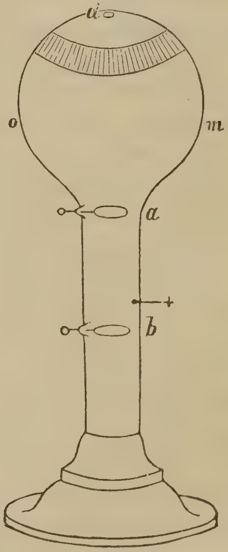


Fig. 4.



If any body be placed on the path of the kathode-rays a shadow is formed on the opposite glass side, which appears evident if the rays consist of moving particles of bodies which proceed in straight lines. As, moreover, many of these particles will collide with each other, some of them must be diverted sideways from the direct course of the rays and produce phosphorescence, though feeble in the shadow of the body. The phosphorescence in the electrical shadow can also be very bright if a body be placed in it which is sensitive to phosphorescence, such as diamond or any sulphur compound. The apparatus in fig. 4 serves to demonstrate this phosphorescence in the electrical shadow.

At *d* a splinter of diamond is stuck on by means of gum, and the mica plate *a* serves as the body producing the shadow. The rays which pass between the plate of mica and the glass side produce on the globe a bright phosphorescent ring, in the centre of which, in the shadow of the mica plate, the diamond splinter too shines manifestly in consequence of the particles of the electrodes turned on one side from the kathode-rays.

In conclusion I will try to give an explanation of the phenomena of phosphorescence.

In the sense of the æther theory of electricity, to be afterwards discussed, on which Franklin, Secchi, Edlund, and others have tried to explain several electrical phenomena, the negatively electrical particles of the electrode have a deficiency of æther. Certain parts of the glass tube will be generally positively, others negatively electrical, or, perhaps too, behave indifferently; that is, they have either an excess or a deficiency of æther, or else a normal quantity. A twofold effect will result from the collisions of the negatively electrical particles of the electrode with the glass sides. *Firstly*, in consequence of the impacts of the particles flying with great velocity, the particles of glass are set in a vibratory motion which will manifest itself as *heat*. *Secondly*, the relative excess of æther (difference of potential) will be equalized between the part struck and the colliding particle of the electrode, causing a concussion in the envelopes of æther of the molecules. If the spot struck and the colliding particle of the electrode have equal quantities of æther, no equalization and only a concussion of the envelopes of æther takes place, which is the more energetic the stronger are the discharges of the electrical current. Just as a calm surface of water struck by drops of rain becomes covered with little ripples, so each point of the glass side struck becomes the centre of waves of æther which we see as phosphorescence. As further, differently stretched strings of an æolean harp are set in vibration by a current of air, and each of them gives a note corresponding to its tension, so also each phosphorescent body shines with the light peculiar to it, dependent on its inner structure and the state of density of the æther. At low degrees of rarefaction, however, the particles of the electrode during their motion meet with many molecules of gas, and after they have partially interchanged quantities of æther meet the glass sides, the latter will either not phosphoresce at all or only slightly, whereas the envelopes of æther of the molecules of gas struck are caused to vibrate, and the gas shows the phosphorescence peculiar to it. The luminous phenomena of gases in Geissler's tubes were for long erroneously considered, according to Plücker and Hittorf, as a luminosity of glowing gases. The more exact investigations of Prof. Hittorf* have, however, shown that we have here merely to do with phenomena of phosphorescence. Experiments of Prof. E. Wiedemann in this direction showed that the temperature of the luminous gas in the tube used by him must be under 60° C.

If the tube be subjected to a strong phosphorescence for at least a minute, it shows in a perfectly dark room after breaking the current a white after-luminosity for about 5 to 6 minutes.

It may be here, too, remarked that the envelopes of æther also are set in vibration when the particles of the electrode are detached, and these latter therefore must become luminous before they collide with particles of gas or side of the tube. It can be explained in this way that the "dark space" is not absolutely but only relatively dark, since the particles of the electrode themselves produce a blue phosphorescence.

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* Wiedemann's *Ann.* vii. p. 580 [*vid. supr.* p. 250].

Rectilinear Propagation of Radiant Electrode Matter and Shadows of Irradiated Bodies.

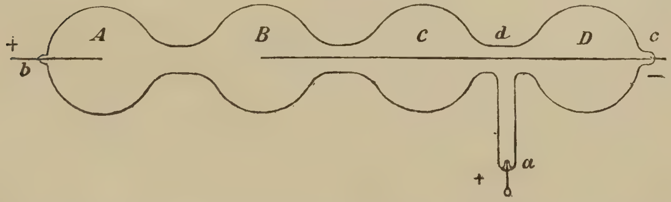
The property noticed by Mr. Crookes that radiant electrode matter moves in a straight direction and throws a shadow of a body irradiated by it on to the opposite glass side, had also been observed by Prof. Hittorf. He proved the rectilinear motion by means of a tube bent at a right angle *, and writes as follows about the shadow :—" Any solid or liquid, whether insulator or conductor, which is in front of the kathode shuts off the glow-light which lies between it and the kathode; there is no deflection from a straight line." If in such circumstances " any object is interposed in the space filled with glow-light, it throws a sharp shadow on the fluorescent side, since its surface just cuts off the luminous cone proceeding from the kathode as apex."

In the same place is further observed, "If the glow-light spreads out in right lines from the points of the kathode, it must be independent of the direction of the positive rays."

At high degrees of rarefaction, however, the irradiation of electrode matter is, as I have often noticed, stronger on the side of the negative electrode plate facing the anode than on the opposite side. Moreover, the radiation seeks the spot on the kathode which lies nearest to the anode.

In a bulb-tube, of the shape represented in fig. 5, in which one electrode *c* was about 15 cm. long, phosphorescence of the glass tube was seen at a certain rarefaction along the whole length of the electrode *c*, and independently of the position of the positive electrodes *a* and *b*. At a greater rarefaction the phosphorescence receded into the bulbs B

Fig. 5.



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* Poggendorff's *Ann.* cxxxvi. p. 8 [*vid. supr.* p. 116].

and C and finally into B alone, if the positive pole were at *b*. If *a* were made the positive pole, the phosphorescence in B disappeared, and the part *d* of the connecting tube nearest to the anode *a* showed a very bright phosphorescent spot.

In this tube I also noticed very sharp alternately dark and light phosphorescent lines wound obliquely like a screw round the electrode as axis covering the glass side as far as the electrode extended.

By using as negative electrode a wire about 4 cm. long, twisted 20 times about its axis, I obtained at the surface of the bulb A, as far as the electrode extended, a number of light and dark circular lines parallel to one another, their plane being perpendicular to the electrode. I thought therefore that these lines were formed in consequence of microscopically small inequalities in the surface of the wire.

The impression of a coin on the platinum foil when used as an electrode only gave a very indistinct and blurred image.

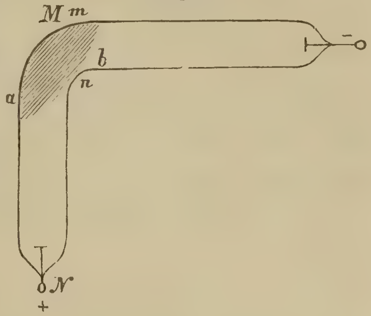
If the radiant electrode matter which causes the phosphorescence consist of material particles, it is not apparent why, in general, no reflexion takes place at the side and why, too, it should not turn round a corner. It is a matter of course that no reflexion takes place in those cases in which the particles of the electrode attach themselves to the glass sides; but as aluminum forms no, or, at any rate, only a very slight deposit, which very probably arises from particles of other metals contained in the aluminum, the electrode matter will bend round the corner and fill the bent part of the tube as a blue light. A reflexion and divergence from the straight direction must also take place with particles of platinum and other metals if they strike with a very great energy, which, after the blow, can overcome the attraction of the glass side on the particles of metal. The material thus reflected will, however, only cause feeble phosphorescence by a fresh collision with the glass side, for its particles have already for the most part neutralized their electrical charges, and have also lost something of the energy of their molecular motion.

The particles of the electrode will move after their reflexion in one, or in all possible directions, according as their velocity is great or small respectively, which latter will be the case for the most part after reflexion.

I will explain here a phenomenon of phosphorescence which Dr. Goldstein* has misunderstood, and which has led to the assertion that the anode light, at any rate at very small densities, has the same properties as the kathode light, namely a rectilinear propagation and phosphorescent action.

We see from the following how Dr. Goldstein arrived at this :—

Fig. 6.



If the positive light fills a strongly evacuated bent cylindrical tube, a bright phosphorescent surface is seen at the outer side of the bend, a semi-oval of parabolic shape. The sharply marked vertex *a* is turned towards the positive end of the tube. On the opposite side *b* turned towards the kathode, the definition fades away. The surface with its sharply marked end extends a little towards the positive side, beyond the extension of the sides of the negative limb.

If several such bends be made in the discharge-tube, a similar phosphorescent surface appears at the outer side of *each* bend. It follows from this on Goldstein's view that it is not the kathode rays, but the *positive light* itself which causes the phosphorescence, for the kathode rays can "at most cause a luminosity at the first bend, but not extend beyond the first bend on account of their rectilinear propagation."

Wires suitably fixed give sharp shadows on the phosphorescent sides, and their position shows that the phosphorescence is excited by rays which "extend very near and parallel to the side of the tube *from the side of the kathode towards the positive side.*"

By experiments made with tubes with several bendings, Goldstein arrived at the following result :—"The *positive* light of a highly rarefied gas consists of rectilinear rays which are transmitted from the positive to the negative side. The rays form a slightly conical brush, whose axis is the axis of the cylindrical tube ; where this brush cuts the side of the vessel, the parts of the rays immediately adjacent to the side cause phosphorescence in it."

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* *Neue Form elektrischer Abstossung von Dr. Goldstein.*

The phenomenon of phosphorescence described by Dr. Goldstein is not caused by the "positive light" but by the particles discharged from the *negative* electrode which strike the glass side *am* (fig. 6) at different angles of incidence, after their rectilinear motion through the negative (horizontal) limb. If we consider, moreover, the circumstance that the phosphorescence of the glass side must be fainter the more obliquely the kathode rays strike it, it is evident that the kathode rays cause a bright and sharply defined phosphorescent surface at *a*, which gradually loses its limit and intensity towards *m*. It is no less easily explained, why the outlines of the phosphorescent surface must be somewhat beyond the prolongation of the negative (horizontal) limb of the tube, because the particles of the electrode mutually repel each other and diverge from their rectilinear paths.

It may be observed in connexion with this, that Mr. Goldstein's remark is not correct when he states that "the kathode rays cause at most a luminosity at the first bend, but cannot extend beyond this," because the particles of the electrode experience reflexion at each bent point (*a m*) of the tube, and must therefore also give rise to a similar phosphorescent surface at the outer side of *each* individual bend.

If the tube near the negative electrode has become coated with a strong metallic mirror, this acts at a greater rarefaction as an electrode. The discharges of the current proceed from the electrode to the surface of the mirror, and from this into the interior of the tube. As, however, the particles of the electrode only hang loosely on the glass side, they become raised to redness and volatilized by the metallic particles striking against them, partly by this motion of heat, partly mechanically by discharges which take place from the glass side into the interior of the tube. If the current be strong (8 cm. spark), red fiery rays are seen to shoot out with a crackling noise from the sides of the mirror perpendicular to the surface towards the middle of the tube, and the tube is flooded from time to time with a blue glow-light, accompanied by a simultaneous disappearance of the phosphorescence of the glass. Platinum electrodes are most suitable for this, since they give a very strong mirror.

As already observed, bodies which are illuminated by electrode matter throw a shadow on the phosphorescent glass side. If the body be turned round about, a much more vivid phosphorescence appears in place of the shadow, and a bright image is seen upon a less bright ground. Mr. Crookes gives an explanation, which is physiological rather than physical, by saying that the glass becomes insensitive by the bombardment of molecules of radiant matter, and "tired by the enforced phosphorescence"*. I think, however, that the cause is to be sought in the fact that, after repeated experiments, the glass side becomes really coated with metallic particles, and hence the phosphorescence is feebler. The phosphorescence must also decrease in consequence of strong heating of the glass side; a faint heating would only make the phosphorescence still brighter.

In the apparatus represented in fig. 7 a mica screen in which a star is cut out is suspended at one side of the plate-shaped electrode of aluminum. The star is suspended at some distance on the opposite side of the electrode, and on irradiation by means of electrode matter a bright star is seen on a dark ground, and on the opposite wall a dark star on a bright ground.

Fig. 7.

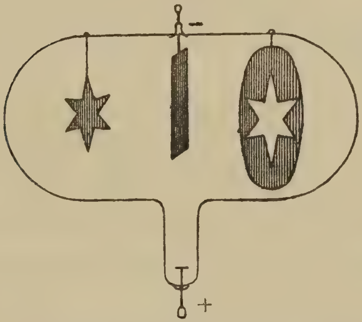
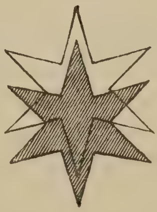


Fig. 8.



If the experiment be so arranged that, whilst the current is closed, a magnet simultaneously deflects the rays, they will also fall obliquely about the edges and meet dark spaces of the glass side. The sharp contours of a brighter and less bright star are *simultaneously* seen which partially cover each

[* 'Nature,' vol. xx. p. 419, 1879.]

other (fig. 8). The inversion of the shadows thus depends not upon the "insensitiveness" for impacts, but upon the fact that the glass side in the shadow is still kept clean, whereas at the exposed parts it is covered with metallic particles.

Thermal and Luminous Action of Radiant Electrode Matter.

If a plate-shaped electrode be curved, the particles which proceed from it perpendicular to the surface will meet in a focal line or focus according to its curvature. The points of union lie beyond the centre of curvature of the surface. I thus determined experimentally the position of the point of union of a hemispherical cup of diameter r to be at a distance $1{\cdot}7\ r$ from it. In these points of union of the rays the particles of the electrode collide with great violence, and a large part of the energy of their progressive motion is changed into atomic motion. So much heat is there generated, that even difficultly fusible metals are melted. In this way Mr. Crookes has melted platinum, iridium, and glass. But Prof. Hittorf, too, has described these fusion experiments in his second communication[*]. He experimented with wire-shaped electrodes. At a distance of 1 to 2 mm. from the negative electrode the positive platinum wire became incandescent and fused to a globule. It is self-evident that this fusion could not take place at a greater distance, for the electrical particles mutually repel one another, and disperse at a greater distance from the point-like end of the electrode.

It naturally suggested itself to raise a solid body to a white heat and *incandescence* by means of radiant electrode matter, and to utilize this for a lamp. I have succeeded in constructing such a lamp, giving a very beautiful and bright light; and although little suited for practical objects on account of the smallness of the source of light, it is still a beautiful experiment[†].

The lamp (fig. 9) has the form of a glass flask, and is furnished with a spherical aluminum cup of 21 mm. radius, which serves as negative electrode. At a distance of 36 mm.

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[*] Poggendorff's *Annalen*, cxxxvi. pp. 210, 211 [*vid. supr.* p. 147].

[†] Since Spottiswoode constructed an inductorium giving sparks a metre in length, it has been possible to raise larger pieces of carbon to incandescence, and to use the lamps for purposes of illumination.

from it is a small cone of carbonized paper, which is fastened by means of a thick platinum wire and a glass rod to the plate-shaped positive electrode.

Paper which has been very carefully carbonized, and even raised to a white heat, still contains, after cooling, very much occluded gas, and in order to remove this and to raise the carbon to a red and afterwards to a white heat the flask must be exhausted for many hours, applying at the same time a strong induction-current of about 10 to 12 cm. spark. During this process it is interesting to observe the spectrum, which shows rays of a greater refrangibility the more strongly the carbon glows. At a white heat the carbon shows a perfectly continuous spectrum. If it is thin and the lamp be surrounded with an opal globe, a faint flickering of the diffused light is observed. If the point-like source of light be examined in a mirror which is oscillated about one of its edges with the hand, an elliptical red band is seen (fig. 10), showing at different points very bright images of the white-hot flashing carbon, covered at one side with a blue glow-light.

Fig. 9.

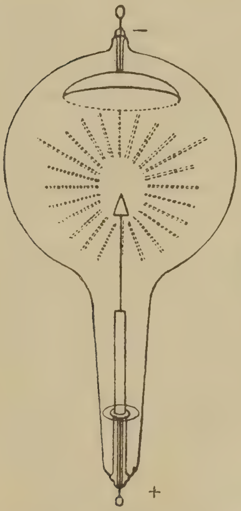
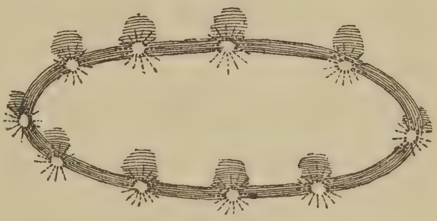


Fig. 10.



The white heat of a thin carbonized paper is therefore not continuous but intermittent; it is raised to a white and diminished to a red heat at each discharge of the induced current. Even after long use the carbon does not show the least disintegration or waste.

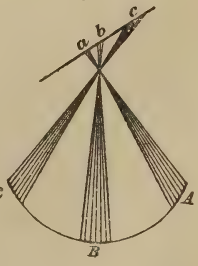
If a carbon so prepared be irradiated by the discharges of a weak induced current (2 cm. spark), it shows on its surface the bluish-green phosphorescence of the diamond already mentioned.

A larger piece of carbon is only brought to a glow at that point which is in the focus of the rays. If the focus be displaced to another spot in the carbon by means of a magnet, so much gas is at once set free that the lamp is extinguished and the carbon is raised to a red heat only.

For this experiment the rarefaction only needs to be about 0·04 mm., at which pressure the most beautiful white glow is maintained. At a further rarefaction, the intensity of the light diminishes, and the phosphorescence of the glass side increases. If the discharge of the induction-current takes place along the glass side, the light is extinguished, the lamp shines in a very beautiful green phosphorescent light, and the cone of carbon only glows faintly at the apex. At a still greater rarefaction the carbon does not glow at all, all the rays pass along the glass side and cause a brilliant phosphorescence.

The discharges along the glass side are ordinarily accompanied by a crackling noise, and not infrequently by a strong flickering, or rather whirlpool-like waving of phosphorescent light; the former is caused by the feeble discharges which take place from the wires and sides of the glass into the air, and also from the trembling motions of the electrodes; the reason for the latter may be that the discharges fluctuate about certain places on the kathode.

Fig. 11.



In order to cause larger pieces of carbon to glow, a leaf of carbonized paper was fixed at 45° to the vertical in the focal line of a cylindrical electrode of aluminum of 20 mm. radius.

A cylindrical electrode was formed with a piece of aluminum foil 3·2 cm. × 2·5 cm. As the carbon was not fixed exactly in the focal line, three focal lines were formed, which are to be explained by the fact that the discharges of the current (10 cm. spark) were not distributed equally over the whole surface of the electrode, but took place at the three positions A, B, C (fig. 11), which was also evident from the phosphorescence on the glass sides.

If the current were interrupted, the red glowing focal lines disappeared immediately. This, as well as the diminution to a red heat of the white-hot carbon referred to, proves that at this high degree of rarefaction, at which the thermal conductivity of the gases can only be small, *the radiation of heat must be very considerable, that thus the constant of thermal conductivity given by the experiments must not only be considered as the measure of the thermal conductivity of the gas but also due to a no small radiation of heat in a vacuum.*

Electrostatic and Electrodynamic Action of Radiant Electrode Matter.

The interaction between the glow-light and a magnet has already been investigated by Plücker, and in a very exhaustive and exact manner by Prof. Hittorf; Mr. Crookes's work, therefore, in this direction can offer us nothing new, with the exception of the conclusions he has deduced from his experiments, to which, however, I cannot assent.

Mr. Crookes admits that, in less strongly rarefied spaces, the discharge passes from one pole to another "carrying an electric current as if it were a flexible wire," but disbelieves that the current of radiant electrode matter from the negative pole carries with it an electric current.

Mr. Crookes believes he has found a proof of this by producing two currents of radiant electrode matter close to one another on a phosphorescent screen, and shows that they mutually repel each other. He then says—"If the streams of radiant matter carry an electric current, they will act like two parallel conducting wires, and attract one another; but if they are simply built up of negatively electrified molecules they will repel each other"*.

The truth lies between the two. The radiant electrode matter consists of particles charged with negative electricity, which, moving with a very great velocity in a straight direction, convey the electricity *convectively*, and effect the conduction of the current between the two poles. If two such particles, charged with statical electricity, were at rest, they must repel each other according to Coulomb's law; and if they were endued by any cause with motion in the same direction, it is not apparent why, during this motion, they should behave differently *towards each other*. Any two negative electrical particles moving in the same direction, thus also any two parallel currents of radiant electrode matter, would therefore repel each other according to Coulomb's law in distinction to galvanic currents which, according to Ampère's law, mutually attract each other.

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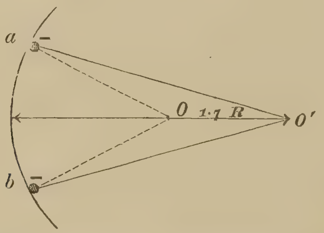
* 'Nature,' 1879, p. 438.

The assumption that the particles of the electrode are charged with *negative statical electricity* explains the repulsion of two parallel kathode rays observed by Mr. Crookes as well as the phenomenon mentioned on p. 260, that the kathode rays emitted from a hemispherical cup do not come to a focus at the centre of the sphere but at a greater distance, which, as my experiments have shown, is at a distance of 1·7 times r from the centre of curvature. It can readily be seen that

Fig. 12.



the particles of the electrode issuing from the points a and b, by mutually repelling each other, cannot meet at the centre O but at somewhere about O', and that the distance OO' will be greater the greater the repulsion between the particles of the electrode.

It is just as easily explicable that the phenomenon of a body irradiated from the kathode gives a *wider* shadow upon the opposite side when itself negative than when it is not electrified, as Dr. Goldstein has observed in an apparatus represented in fig. 13. If in the latter the aluminum wire $a\ a$

forms the negative electrode, an equally stout aluminum wire *a′ a′* gives a narrow shadow on the opposite side, which at once becomes wider if the eyelet *a* be connected to *a′* by a wire. In the first case the particles discharged from the kathode *a* pass the wire *a′ a′* without being diverted from their rectilinear path, and the shadow *mn*, fig. 14, is formed on the opposite side. If, on the other hand, *a′a′* itself be negatively electrical, fig. 15, the approaching particles will be diverted and move in bent directions *a a′ m* or *a a′ n*. The wire *a′ a′* irradiated by *a a* gives a shadow *m n* on the opposite side (fig. 15); and since, moreover, *a a* is also irradiated by *a′ a′*,

Fig. 13.

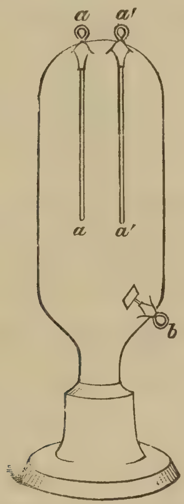


Fig. 14.

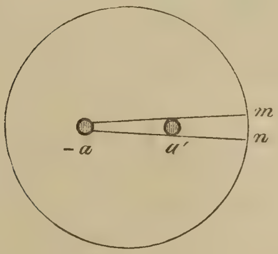
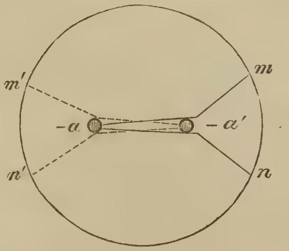


Fig. 15.



the wire $a\,a$, too, gives a wide shadow $m'\,n'$. The parts of the sides $m\,n$ and $m'\,n'$ are, however, irradiated respectively, too, by $a'\,a'$ and $a\,a$, owing to which the shadows are only relatively and not absolutely dark. The parts of the sides $m\,m'$ and $n\,n'$ are simultaneously irradiated by both electrodes $a\,a$ and $a'\,a'$.

Dr. Goldstein, in his comprehensive paper, entitled "*Eine neue Form elektrischer Abstossung*," has described this experiment with the electrical shadow without having explained it.

It may here be remarked, that two currents of radiant electrode matter would very probably also attract one another if the velocity of motion of the particles of the electrode were of the same order as that of electricity in solid conductors. At a lower velocity the electrodynamic action is overpowered by the electrostatic action. On the other hand, by the interaction of galvanic currents, the electrostatic repulsion disappears in comparison with the electrodynamic attraction, but is not equal to zero, as the experiments of Herwig show*. He found that the electrodynamic attraction of two coils was different according as both were inserted in the same circuit close to the same, or to different poles. The electrodynamic attraction is somewhat smaller in the former case than in the latter. The coils in the first case are charged with similar free electricity, and the electrodynamic attraction is weakened by the electrostatic repulsion; in the latter case both actions add themselves, because the electrostatic charges of both coils are dissimilar.

That the currents of radiant electrode matter nevertheless represent actual electric currents is shown by their electromagnetic behaviour, which follows the same laws as the action of galvanic currents. *The mutual repulsion of two currents of radiant electrode matter can only hold as a sure proof that the electric current is caused by the transport of particles electrically charged, and that we have here the case of an electrical convection of a molecular conductor* analogous to that electrical convection of solid conductors which, as the beautiful experiments of Prof. Rowland show, is, electrodynamically considered, equivalent to the flow of electricity in the conductors themselves.

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* Poggendorff's *Annalen*, cxlix.

It can scarcely be doubted, moreover, that the same laws will hold for the convection of molecular conductors as for that of solid conductors. Each particle of the electrode charged with statical electricity which is in progressive motion will behave in the same way towards a magnetic pole as a positive electrical current flowing in the same direction as the positively charged particles, or in the opposite direction to the negatively charged particles. Every electrical particle which traverses a certain path represents to us in reality an "*elementary current*," which up to the present we have used as a mathematical magnitude in our electrodynamical calculations.

Since, as we have already seen, the particles of the electrode are negatively electrical in the rarefied space and move from the negative pole, the action of the current caused by molecular convection is the same as that which would be exerted on a magnetic pole by a positively electrical current flowing in the opposite direction to the motion of the negatively charged particles, that is, from the positive to the negative pole.

I firmly believe, too, that the laws here mentioned can be verified by experiment. For example, an electrified current of steam passing through a tube must deflect a magnetic needle in a way which results from the above consideration. I hope shortly to be able to carry out experiments in this direction, and I will only mention here that I am confirmed in my conviction of the correctness of the above view by an experiment of Mr. Donato Tomasi*, who magnetized an iron cylinder by passing a current of steam, at a pressure of 5 to 6 atmospheres, through a copper tube of 2 to 3 mm. diameter, coiled spirally round the cylinder.

In a notice relative to this in the *Annalen*, Poggendorff remarks :—" In order that this experiment may succeed, however, the conditions must probably have been fulfilled which Faraday has stated to be necessary for the proper electrification of the current of steam."

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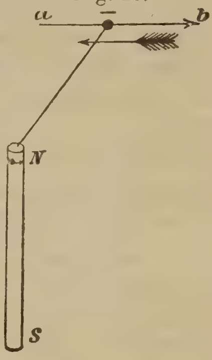
* Poggendorff's *Annalen*, clv. p. 176.

I consider it very probable that Mr. Tomasi observed the electrical convection of molecular conductors.

Let us suppose a plane through the direction of motion *a b* (fig. 16) of the negatively electrical electrode particle and the pole of the magnet *N* (let it be the plane of the paper), then the particle during its motion represents to us a positive elementary current in the opposite direction, which is given by the arrow below, and the interaction between the elementary current and the north pole must be measured analogous to the law of Biot and Savart by a couple of forces which are perpendicular to the plane *a b N*, and the intensity of which is inversely as the square of the distance between them as well as directly proportional to the sine of the angle which the momentary direction of motion *a b* forms with the polar direction, the strength of the magnetic pole, the quantity of electricity, and the velocity of its motion.

Fig. 16.



From Ampère's rule it can further be deduced to which side of the plane chosen (*a b N*) the particle will be deflected. If the pole is north magnetic the electrode particle will be deflected to the right for an observer looking towards the pole and swimming with the imaginary positive current.

On the other hand, if the observer of the north pole moves in the same direction as the electrode particle, the latter will be deflected to the left.

As, moreover, for a finite magnet the tangents to the magnetic curve, which pass through the electrode particle, represent the direction towards the pole, the force which deflects the particle is perpendicular to the plane which can be drawn through the direction of motion of the particle and the magnetic curve of its transitory position at the moment of observation.

All interactions between the magnet and a current of electrode matter can be explained and predicted by the laws of electrical convection of molecular motion with the aid of Ampère's rule.

Some simple cases are here discussed.

1. The pole of the magnet *n* and the particle of the electrode *m*, the latter moving to the right with a very great velocity in the direction of the arrow, are both in the plane of the paper. The pole imparts a small velocity to the particle under the plane of the paper or on the left side of the observer who sits on the particle of the electrode and looks towards the *n* pole. The particle will move with the resultant velocity *m r* under the plane of the paper, and will diverge the more from the original direction the stronger the magnetic action and the smaller the velocity with which the particle is projected from the electrode. With a south pole the direction of motion falls in front of the plane of the paper.

Fig. 17.

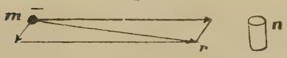
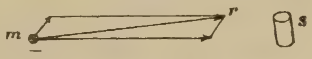


Fig. 18.



2. The pole of the magnet *N* and a section of the tube from which the particles are issuing in a direction normal to it, are in the plane of the paper. Each particle receives a deflection in the direction of the small arrows; the light, therefore, is displaced to one side. In fig. 20 the particles move normally under the plane of the paper, and therefore invert the directions of their motion. With a south pole the phenomena are inverted in both cases.

Fig. 19.

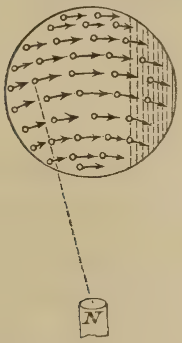
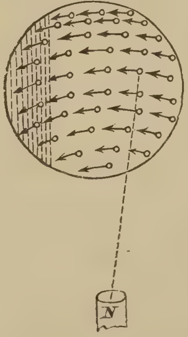


Fig. 20.



3. From what has been said, the following figures are

easily intelligible. The action of both poles imparts to the particle of the electrode in the first case a resultant velocity *m r* downwards, in the second upwards. Thus the particles

Fig. 21.

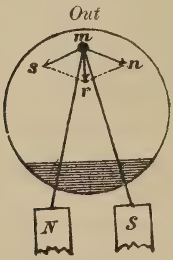
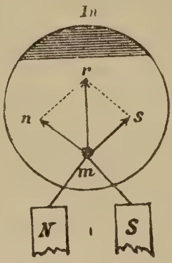


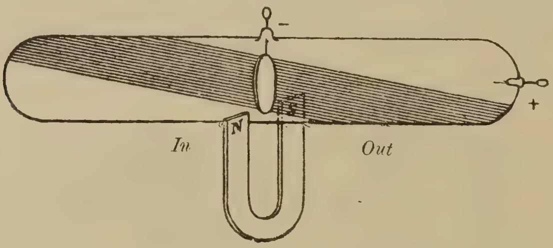
Fig. 22.



are diverted from their original direction of motion in the first case downwards, in the second upwards.

Fig. 23 represents both cases in one tube, in which the particles are projected from the plate-shaped electrode in opposite directions.

Fig. 23.



4. If the initial velocity of the electrode particle is small, as is the case at a greater pressure in the dark space of the *glow-light*, it will be very strongly deflected from its original direction, and since the action of the magnet is a continuous one, the direction of the path of the particle will be always changing. The particle moves according to the position of its direction against the lines of force of the magnet in curves of a simple or double curvature. In fig. 24 the particle *m* is projected in a direction *ma* at right angles to the line of force *m*N, and rotates in the direction of the molecular current of the pole, so that the line of rotation is perpendicular to the line of force. If the initial velocity forms an acute

or obtuse angle with the line of force, the direction of the rotation remains the same; but the plane of rotation changes

Fig. 24.

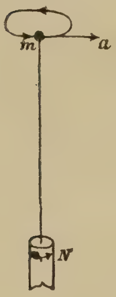


Fig. 25.

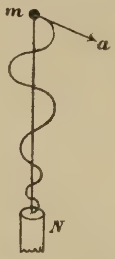
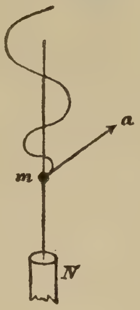


Fig. 26.



continuously, and a path of double curvature is formed, which, on account of increasing magnetic action, is more strongly curved towards the bottom.

5. From a pointed electrode the particles are projected in divergent directions, and on approaching a north pole wind themselves about a cone whose apex is turned towards the north pole, and whose axis coincides with the line of force of the point-shaped electrode. In this is to be found the explanation of the beautiful phenomena in the glow-light, which Prof. Hittorf obtains with the aid of strong magnets. I will here give the drawing of his experiments, which represent the three cases discussed above.

The wire-shaped electrode is surrounded as far as the last section with a glass tube and in fig. 27 (p. 272) is perpendicular to the vertical line of force, therefore in the middle of a circular luminous appearance. If the magnet is very strong, the cone of light contracts to one line, and the rotation of the luminous particles can no longer be distinguished.

Since only a few rays diverge from the last section of the electrode, the spiral turns in the upper and lower parts of the cone of light can scarcely be seen. On the other hand, the convolutions appear very beautiful and distinct if the pencil of rays forms an acute or obtuse angle with the line of force, as is shown in figs. 28 and 29.

Fig. 27.

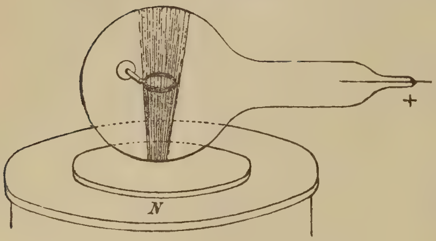


Fig. 28.

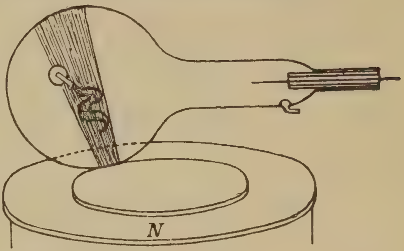
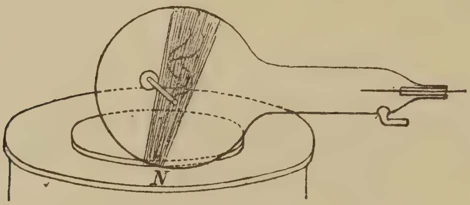


Fig. 29.



6. The magnetic surfaces of the glow-light observed by Plücker can be just as easily explained, by which is understood those surfaces to which the glow-light is spread out under the influence of a strong electromagnet, and which are formed by the whole of the magnetic curves passing through the single points of the negative electrode and both magnetic poles.

Fig. 30.

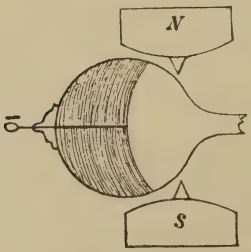
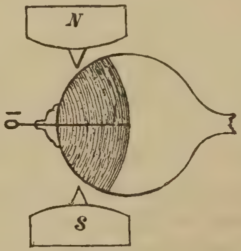


Fig. 31.



Both poles and the negative electrode lie in the plane of the paper. The particles emerge from the wire-shaped electrode radially in all directions perpendicular to the axis.

Those particles which are emitted from the wire upwards or downwards perpendicular to the plane of the paper are perpendicular to the lines of force which pass through the electrode. These particles must therefore rotate about the line of force in very small circles in a corresponding direction to the molecular currents of both poles. All other particles which emerge from the electrode, obliquely to the plane of the paper or in it, form obtuse angles with the lines of force and must therefore revolve spirally about the latter towards the pole and form a surface of light in the plane of the paper.

Thus all phenomena which are shown by radiant electrode matter as well as by the glow-light under the influence of a magnet can be completely explained by those laws which have been experimentally determined for the electrical convection of material conductors, and by induction have been extended by me to molecular electrode particles also. The solution of this problem was rendered feasible by the possibility of determining the direction of motion of the particles of the electrode.

These laws of electrical convection do not, however, appear to apply to the positive brush-light, and the view that the electric current is caused by the motion of the electricity in the column of gas, just as in a stationary solid conductor, appears to be justified by the behaviour of the positive brush-light. Just as in solid conductors, the molecules which produce the motion of heat allow a passage to the current without changing their relative positions of stability, so, too, in gases of a certain density the electricity appears to discharge itself from section to section without altering thereby either the uniformity of their molecular motion or other oscillatory motions.

The positive brush-light behaves therefore towards the magnet like a very easily flexible wire which is conveying a positive current flowing in the same direction as the column of air. If the brush-light be stratified the stratifications are compressed by the magnet to that side of the tube indicated by the law of Laplace.

If alternating currents are transmitted, it is easily seen that the negative light collects in Plücker's magnetic surface, and the positive light in an equatorial plane perpendicular to this surface, and the phenomenon observed by Prof. Reitlinger and v. Urbanitzky is obtained which I call a triple surface (*Dreifächerfläche*), because it shows three surfaces which are perpendicular to one another. On inverting the current the positive surface must appear on the opposite side of Plücker's surface and the treble surface appears to have undergone a rotation of 180° about the wire kathode [*].

Phenomena of Motion in Radiant Electrode Matter.

After we have recognized the existence of radiant electrode matter, the explanation of some of the phenomena of motion caused by it in exhausted vessels will offer no difficulty. Mr. Crookes describes some little forms of apparatus, of which the fly-wheels were moved by means of radiant electrode matter in the direction from the negative towards the positive pole. On inverting the current, the direction of the rotation was also reversed.

The sketch fig. 32 represents an electrical radiometer which I have constructed. A small wheel of unblackened mica is suspended on a needle-point by means of a small glass cap, and two flat electrodes are fused excentrically into the glass vessel. To obtain a stronger action the electrodes were bent cylindrically, so that their focal line fell on about the middle of a wing when the latter was between the two electrodes.

Fig. 33 represents the section of the apparatus : the small wheel revolves in the direction of the motion of radiant electrode matter, from the negative towards the positive pole.

Prof. F. Zöllner describes an experiment in the third paper of his "*Untersuchungen über die Bewegungen strahlender und bestrahlter Körper*," which Geissler communicated at the last *Naturforscherversammlung* in Hamburg, and which he himself repeated with equal success [†]. Two platinum wires were fused in as electrodes, and the movable cross consisted of unblackened mica laminæ. If the induced current of a small Ruhmkorff's apparatus were passed through the vessel at a tension of 1 mm., the cross rotated always in such a direction "as corresponds to an emission of material particles from the *positive* electrode. On inverting the current, the direction of rotation of the cross changes."

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[*] *Wien. Akad. Anzeiger*, 1877, no. 10.

[†] Poggendorff's *Annalen*, clx. p. 464.

Fig. 32.

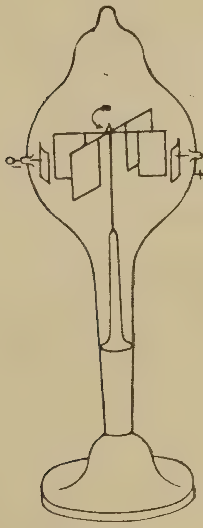


Fig. 34.

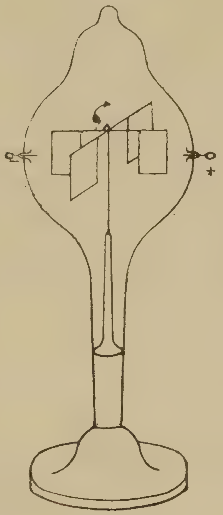


Fig. 33.

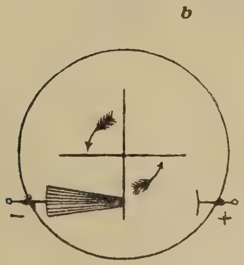
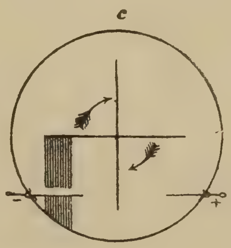


Fig. 35.



It was of great interest to me to determine whether this rotation in the direction of the emission of the particles from the positive electrode also took place at a pressure at which the radiant electrode matter appears. I made the experiment with a radiometer represented in fig. 34, which is furnished with two wire electrodes. At a pressure of 0·03 mm. the little wheel revolved in a direction opposite to that in which it would have rotated with flat electrodes.

The question now arises: Are the particles emitted from the positive or negative electrode, and how is that inversion of the direction of rotation to be explained?

This question is solved by the following very simple experiment.

If an induction-current be passed through a cylindrical glass vessel into which a long wire reaches almost to the middle, on using this as a negative electrode the vessel shows a phosphorescent equatorial zone (fig. 36), which luminous phenomenon assumes an oblique position, as regards the electrodes, as soon as a horseshoe magnet is placed about the glass vessel in the manner represented in fig. 37 and fig. 38.

The luminous equatorial zone can only be formed by the particles of the electrode being emitted perpendicularly to the axis of the wire in all directions. That, too, the last section of the wire emits particles perpendicular to the surface is self-evident, only their number is very small in proportion with those thrown off sideways.

Fig. 36.

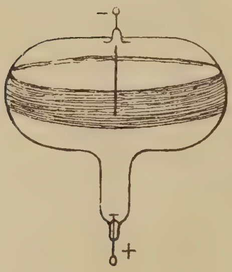


Fig. 37.

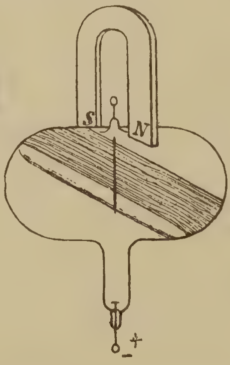
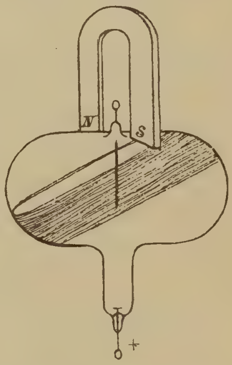


Fig. 38.



It is now easy to understand why, with the same direction of current, the small wheel in the radiometer with wire electrodes turns in the opposite direction to that with plate electrodes. It is at once evident from the sketch, fig. 35, that the lateral emission of the wire must turn the wheel in the opposite direction.

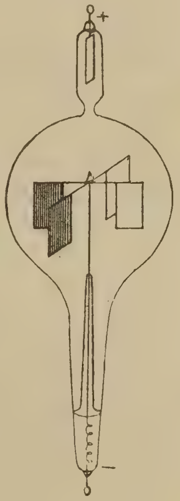
At a very high degree of rarefaction (0·01 mm.) the wheel *turns round* and rotates in the direction of the emission of particles, from the negative towards the positive pole. This is explicable by the fact that at this rarefaction the emission of the particles only takes place at the last *cross section* of the wire.

Thus an emission of the particles does not take place at the positive, but only at the negative pole, and always normal to the surface of the kathode.

That the same explanation holds good for the inversion of the direction of rotation at a pressure of 1 mm. is self-evident, since we have seen that at this degree of rarefaction also particles are emitted from the negative electrode which, diffusing into the residual gas, cause it to phosphoresce, and are therefore unable to cause phosphorescence of the glass side.

The phenomena of motion are more complicated in the electrical radiometer described by Mr. Crookes, represented in fig. 39. The cross, which rests by means of an iron cap on a needle-point, consists of four aluminum plates coated on one side with mica, and the needle is connected by means of a wire to the platinum electrode which is used as a negative pole. In the upper part of the vessel a second platinum wire has fused to it an aluminum plate which serves as the positive pole. In the radiometer with which I experimented the upper tube was strongly constricted (to about 3 mm. diameter). If this part were touched with the finger during the passage of an induction-current giving a 4 cm. spark at a pressure 0·03 mm., the luminosity disappeared from the interior of the tube and a discharge of the current took place again as often as the part was left free. This experiment only succeeded when the upper wire was used as a negative pole.

Fig. 39.



Mr. Crookes observed in this apparatus with a position of the poles represented in the sketch a rotation of the cross with the mica sides forwards and at a pressure which "is a little beyond that at which the dark space round the negative pole extends to the sides of the glass bulb." The rotation begins at a pressure of about 0·05 mm. This motion Mr. Crookes explains in the following manner[*]:—

"The molecules being driven violently from the pole there should be a recoil of the pole from the molecules, and by arranging an apparatus so as to have the negative pole movable and the body receiving the impact of the radiant matter fixed, this recoil can be rendered sensible."

According to the view of Prof. Hittorf[†] the mill rotates first of all when the hot glow-rays reach the glass sides of the vessel and heat the parts touched. "It is the thermal radiation of the glass side therefore which first causes a rotation."

Neither explanation, however, is correct. The incorrectness of Hittorf's view is easily proved by warming the glass bulb of such a radiometer by touching it with the hand. The little wheel rotates with the aluminum and not with the mica forwards even when no current is passing. Since this experiment has not yet been explained so far as I know, a note about it will follow in a later part of this paper.

For the purpose of refuting Mr. Crookes's explanation I will here describe some experiments I have made with the radiometer referred to.

If care is taken to provide for equal distribution of temperature in the radiometer at a pressure of about 0·2 mm., the little wheel revolves with the aluminum forwards once or twice immediately after closing the current, then stops, turns round and revolves with the mica forwards as long as the current remains closed. If the current be afterwards broken the rotation continues, and for so much the longer the stronger the current has been.

I repeated this experiment very often with the same success. If the experiments follow one another without waiting for an equal distribution of temperature, the wheel always rotates towards the mica face.

At a continued rarefaction the number of the incipient revolutions towards the aluminum face becomes larger and larger and also the velocity of the rotation after the inversion. If the current be broken the wheel rotates with a violence which I have not observed in the most sensitive radiometers. The individual laminæ can no longer be discriminated.

[*] Nature, 1879, p. 436.

[†] Wiedemann's *Annalen*, vii. p. 607 [*vid. supr.* p. 224].

If the pressure is so small that the phosphorescent phenomenon of the glass side is visible, at about 0·04 mm., the wheel only rotates towards the aluminum face and the inversion of the rotation takes place only towards the mica face after breaking the induction-current, and continues for five or six minutes or even longer according to the intensity of the current and duration of its action.

The complete course of these phenomena of motion has not been noticed by Messrs. Hittorf and Crookes, and it has therefore not been easily possible for them to find a correct explanation.

These motions of rotation are regulated by the following causes, opposite in their action :—1. By the emission of radiant electrode matter ; 2. By the motion of heat which the electric current causes in the aluminum plates ; 3. By the radiation of heat from the glass sides.

The reaction of the emitted particles of the electrode must cause a motion of the wheel towards the mica face, according to the principle of the maintenance of the centre of gravity. The same motion must also result from the reaction of molecules of gas striking to and fro on the aluminum side of the wings warmed more strongly by the current. Both forces thus act in one direction.

A third force, acting in the opposite direction to the two first forces, results from the heating of the glass sides by the particles of the electrode striking against them. The glass sides radiate heat towards the interior. The surfaces of the mica and aluminum become warmed, but whereas in the former the heat remains in the highest layer, in the aluminum, on account of its good conducting power for heat, it is transmitted to the lower layers. Hence the surface of the mica becomes warmer than that of the aluminum, and from the reaction of the particles of gas and of the electrode striking to and fro, a motion of the wings takes place towards the aluminum face.

We can easily convince ourselves of this by using a radiometer whose aluminum wings are covered on one side with mica. Fig. 40 on page 281 is the section of such a radiometer. Aluminum is denoted by a dark band. If the glass vessel is warmed by means of the hand or radiant heat of a hot metal plate, dark heat-rays are absorbed in the glass side and only indirectly reach the wings. The heat-motion of the glass sides is conveyed to the vanes by means of radiation and molecular motion of the gas, and these move for the reason given with the aluminum face forwards.

The above three forces act simultaneously on the vanes so long as the current is closed and can mutually in their actions weaken or entirely annul one another. If the current is closed the heating of the aluminum plate is at first very small, the radiation of the glass sides preponderates and causes an incipient rotation towards the aluminum face. After some time the heating by the current continually becoming greater finally obtains the ascendency, and an inversion of the direction of rotation takes place. After breaking the induction-current a rotation takes place in consequence of this heat-action towards the mica face until the temperature in the plates has become equalized.

On continued rarefaction the resistance to the induced current, thus also the energy of the discharges and heating of the glass sides, becomes larger and larger, on the other hand, the resistance of the air, which retards the motion of the vanes, less, hence the number of the incipient rotations towards the aluminum face and in like manner the velocity of rotation towards the mica face increases on closing and opening the current.

At a very small pressure the radiation of the walls is stronger than the heating of the vanes by the current, the wheel *only* moves towards the aluminum face as long as the current remains closed ; after breaking it the surface of the mica plate becomes colder than that of the aluminum, because in the latter the lower strata can give up their heat rapidly to the upper ones and the wheel must rotate in the opposite direction.

Now theory is only correct if the conclusions to which it leads can be verified by experiments. We will therefore submit the explanation of the radiometric phenomena of motion given to this test, and for the sake of simplicity consider a fixed aluminum cross whose vanes are covered on one side with mica. A cubical surface envelope surrounding the cross is movable about a vertical axis. The sketch fig. 41 represents the section of this arrangement and of the case; the black sides of the cross denote aluminum.

At a moderate rarefaction, when the heating of the vanes by the current preponderates, the molecules of gas rebound from the aluminum face with a greater velocity, move with the emitted particles of the electrode against the envelope, and give a resultant pressure in the direction of the arrow at about the middle of the quadrant. The same pressures act also in the other quadrants. The direction of rotation of the envelope is seen from the sketch, and is opposite to the direction of rotation of the movable cross.

Fig. 40.

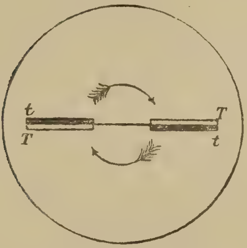
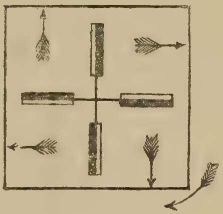


Fig. 41.



At a very high degree of rarefaction, a rotation must take place in the opposite direction if the radiation of the envelope preponderate.

This conclusion from the theory of the phenomena of motion here given has been completely verified by experiment. The radiometer which I constructed for this purpose consisted only of two fixed vanes (fig. 42, p. 282), and a glass globe which was movable on a pivot. At a moderate rarefaction the glass globe rotated in that direction of the emitted particles of the electrode which had been previously determined.

At a greater rarefaction, when the glass globe phosphoresced brightly, a rotation took place in the opposite direction, *i. e.* from the mica side of the one vane to the aluminum side of the next following.

In these and other apparatus I have often made the remarkable observation that if they had been very strongly evacuated and not in use for a long time, phenomena occur for some seconds on the passage of the current which otherwise are seen only at a low degree of rarefaction. While the sides phosphoresce faintly the interior of the apparatus is filled with a blue mist. After a short time this mist disappears, the atmosphere becomes clearer, and the phosphorescence brighter, corresponding to the high degree of rarefaction. The phenomena of motion are such, too, as are observed at a greater pressure. The glass cylinder rotates in the direction of the emission of the particles from the aluminum face, stops after a few revolutions, and afterwards changes its direction of rotation. I explain these changes in pressure in this way, that on the passage of the current the occluded gases are disengaged from the electrodes and somewhat increase the pressure. After some time a portion of the particles charged with statical electricity remains adhering to the glass and is partly absorbed by the positive electrodes, in consequence of which the pressure of the rarefied gas diminishes.

Fig. 42.

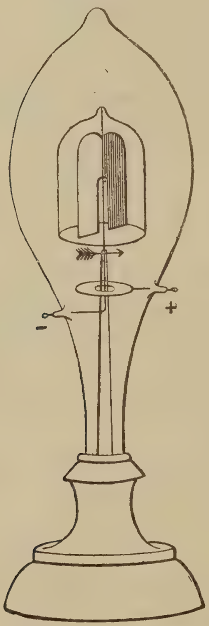
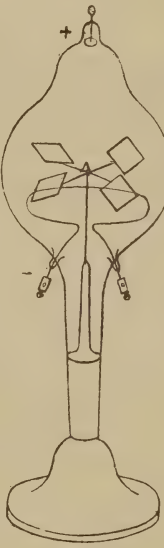


Fig. 43.



Mr. Crookes also describes in his work a radiometer which Prof. Zöllner had already constructed years before and attempted to explain in the treatise alluded to, *Unter-*

suchungen über die Bewegungen strahlender und bestrahlter Körpen *. The apparatus consists of a movable cross with unblackened mica plates which are inclined towards the horizon as is seen in fig. 43. A ring of platinum wire lying horizontally is placed under the cross and its ends are fused into the glass side in order to be able to pass a galvanic current through it.

Reserving the minuter details of all the experiments which Prof. Zöllner carried out with this apparatus for the next paper, I will only allude here to that experiment which Mr. Crookes, to whom Zöllner's work appears to have remained unknown, repeated with like result and explained incorrectly.

If a galvanic current be passed through the platinum ring at a high degree of rarefaction, "normal" rotation of the wheel takes place; that is, such a rotation as might have been explained according to Zöllner's view by an upward current of air or by a process of emission from the surface of the wire †.

The rotation of the wheel in a normal direction is independent of the direction of the current.

Mr. Crookes also describes this experiment and remarks on it as follows :—"Here, then, is another important fact. Radiant matter in these high vacua is not only excited by the negative pole of an induction-coil, but a hot wire will set it in motion with force sufficient to drive round the sloping vanes" ‡.

Mr. Crookes appears to wish to seek confirmation of this view in the following modification of Zöllner's experiment. His radiometer was furnished with an electrode above the cross (fig. 43). If the platinum ring were used as the negative electrode of an induction-current, the wheel revolved in accordance with an emission of the electrode particles in a normal direction, that is, the same direction as that in which it rotates on the passage of the galvanic current.

We are, however, in no way justified in concluding that *similar effects are due to similar causes*, and so much the less since the induction-current in its passage through the platinum ring cannot alone set the radiant matter in motion ; a

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* Poggendorff's *Annalen*, clx. p. 460.

† *Tom. cit.* p. 300.

‡ Nature, vol. xx. 1879, p. 436.

heating of the wire by the galvanic current must first take place if the particles are to be emitted.

The investigations which I have made with Zöllner's radiometer lead, in conjunction with the facts observed by him, to the following simple explanation of this experiment.

At a high degree of rarefaction in this radiometer (0·02 mm. mercury pressure), owing to the smaller thermal conductivity of the residual gas, the heating of the wire is greater and consequently the thermal radiation stronger; the latter according to Stefan being proportional to the fourth power of the absolute temperature *. Thus the mica laminæ become more strongly warmed on the side facing the platinum ring than on the opposite side, owing to their low conducting power for heat; and there results from the impact and recoil of the molecules of gas on the more strongly heated face of the laminæ a pressure on their upper surface directed perpendicularly, which must turn the wheel in the direction observed.

Besides the action of radiant heat, this motion is also caused by the thermal conductivity of the gas. By striking against the hot wire, the molecules of gas acquire a greater molecular velocity, and transfer part of their *vis viva* to the vanes. In the first case the motion is caused by a mere *reaction* of the colliding molecules of gas, in the second by a *transfer of vis viva*, by means of impacts of the molecules of gas. Both actions add themselves, since they take place in the same direction, and hence the violent rotation which is here generally noticed.

In order to test the views here advanced as to the cause of the phenomena of motion, I have constructed a new electrical radiometer. Such a one is represented in fig. 44. The pair of semicylindrical vanes of aluminum foil is suspended free to move by means of a brass cap on a steel point; the latter is in connexion with the platinum wire fused into the glass, and is used as the kathode. The anode is above the fly-wheel in a narrow piece of the tube.

The following phenomena of motion were observed with this radiometer:—

1. At full atmospheric pressure the pair of vanes revolved with the *concave* side forwards, and it was immaterial whether

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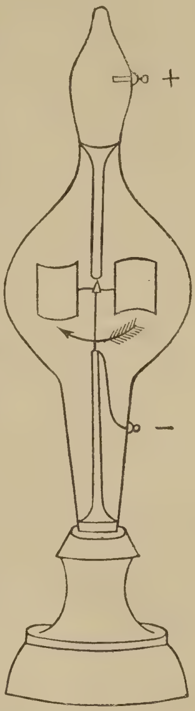
* *Sitzungsbericht Wien. Akad.* lxxix. p. 391.

they were used as anode or as kathode. If the palm of the hand was placed about the pear-shaped glass vessel, but not in contact with it, the pair of vanes revolved very quickly with the convex side forwards, and still more quickly on touching.

Fig. 44.



2. At a pressure of about 620 mm. the first inversion of direction of the vanes took place, and they rotated with the convex side forwards. The velocity of motion on further rarefaction increased at first, and then decreased until the rotation finally ceased, when a streak of light appeared between the metallic cap and the anode. At about 390 mm. the wheel revolved so quickly that the vanes could no longer be distinguished. The motion was somewhat quicker when the pair of vanes was used as the kathode, and slower when as the anode. At about 140 mm. the motion ceased.

3. At a pressure of about 0·5 mm. a second inversion of direction took place if the pair of vanes served as the kathode, and the wheel surrounded by a glow-light rotated with the concave side forwards. At a further rarefaction, the velocity of motion at first increased and then decreased. At about 0·04 mm. pressure the motion was very quick, and at 0·02 mm. considerably slower. The frictional resistance at the point could often not be overcome, and therefore the beginning of the motion had to be assisted by gentle tapping.

At this rarefaction the following experiment was tried. I allowed the current to discharge itself for 30 to 60 seconds through the radiometer until the vanes began to move towards the concave side. If the current were now broken, the vanes rotated rather quickly about twice in a second, and made about 130 rotations; this experiment was often repeated with similar results. At a further rarefaction, the number of rotations was always smaller after breaking the current.

4. At a still further rarefaction of about 0·01 mm., when

the glass sides phosphoresce brightly, a *third* inversion of the direction of motion takes place. The pair of vanes turns once more with the convex side forwards. The discharges take place for the most part only at the edges of the aluminum plates, and hence very many luminous figures which rotate with the vanes appear on the sides. As, moreover, the discharges are intermittent, they strike different parts of the glass side during the motion of the vanes, and, on account of the longer duration of the impression of light, the eye sees them simultaneously. The glass vessel shows a very beautiful play of flickering lines of light. The phosphorescence of the glass sides is somewhat more vivid, and the rotation of the vanes quicker if a break of air is interposed in the conducting wires.

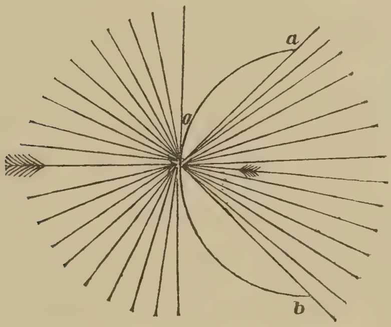
If at this degree of rarefaction the vessel be touched with the moistened finger, or only breathed upon close to the tube fused in above the fly-wheel, the discharge and phosphorescence phenomenon disappear for some time. Moistening the vessel below the wheel does not cause this effect.

I will at this point first explain the third case of all the phenomena of motion, in which the fly-wheel at 0·02 mm. pressure of mercury revolves towards the concave side after breaking the inductive current. Here manifestly *only* the thermal action of the current can be the cause of the rotary motion.

We will now see how a motion towards a concave side can be caused by the equable heating of a semicylindrical aluminum plate. In fig. 45 *a o b* represents the section of such a vane. The molecules approaching from both sides rush back from the equably warmed plate with a greater velocity, and from their reaction against the plate there result two opposite pressures normally directed against the same. For simplicity, we will consider a small element of the surface at *o* on the apex of the vane. At the concave side, only those molecules react on the element of surface which rush away in all directions inside the aperture *a b*. The other molecules will give up the motion received from the element of surface somewhere on the concave side of the plate. A part, so to say, of the moved molecules will be caught on the concave face, and not come into effect.

The resultant of all the reacting forces on the element of surface on the convex side must therefore, as is apparent from the sketch, be greater than on the concave side, and the plate will move with the concave side forwards. Such a fly-wheel, whose temperature is higher than that of its surroundings, thus moves in the same direction as under the action of rays of light, which for the most part, too, are converted into the heat of the metal vanes. The partially *reflected* rays of light unite in a focal line and raise the temperature there. The colder gas streams over the convex side towards the focal line, and carries the vane with it in consequence of the friction, which at this rarefaction is scarcely three times smaller than at the atmospheric pressure. The rays of light reflected and converted into heat act in the same direction.

Fig. 45.



An irradiated or warmed wheel with concave vanes thus moves towards the *concave* side. If, on the other hand, the glass vessel be warmed, for example by placing it in a warm atmosphere, the motion must take place towards the *convex* side.

After this consideration, I proposed the further question whether, and how, a semicylindrical pair of vanes would move when *insulated* from the point by means of a glass cap. If the above view of the thermal action of the induction-current were right, and if there were no other cause of motion besides this thermal action, the pair of vanes must now remain at rest, since the discharges *only* proceed from the metal point.

Experiment, however, did not verify this conclusion. The pair of vanes rotated with the *convex* side forwards, and that too at the most extreme rarefaction, when the glass sides were phosphorescing briskly. After breaking the current a rotation took place in the opposite direction.

Since glass, as is well known, conducts the induction-current tolerably well, the possibility was not excluded that electricity discharges through the metal point, the glass cap, and the wings. I therefore constructed a pair of vanes of semicylindrical mica plates, and insulated them by means of a glass cap from the needle-point. This fly-wheel, too, at an extreme rarefaction showed a motion towards the *convex* side and rotated in an inverse direction when the current was broken.

From this experiment I believe I may conclude with certainty that the motion of the fly-wheel is *indirectly* caused by the particles of the electrode. The particles heat the glass sides, and it is the radiant heat of the latter, and the particles of gas rushing back violently into the interior of the vessel, which cause the motion towards the *convex* face, as in an ordinary radiometer with semicylindrical vanes.

If the experiment lasts a long time, the vanes are gradually warmed, and rotate after breaking the current towards the *concave* face, on account of the quicker cooling of the glass sides.

I will here remark that fly-wheels both of aluminum and mica also rotate at a pressure of about 400 mm. towards the *convex* side, most probably in consequence of faint discharges at the points of the vanes, thus acting as ordinary fly-wheels. At other degrees of rarefaction, the wheels remained indifferent or their motion took place towards one side or the other.

The idea naturally suggested itself, that in Crookes' radiometer, too, the motion towards the aluminum face at an extreme rarefaction, first noticed by me, is due to the same cause, viz. to the *heating of the side* by the particles repelled from the kathode.

For this purpose I have constructed a pair of vanes of very thin brass and mica, and insulated it from the point by means of a glass cap. At an extreme rarefaction the wheel rotated several times, first of all towards the metallic face and afterwards rather quickly towards the mica face. The glass cap rattled on the point so loudly that the noise could be heard in the next room, even when the door was closed. The jumping motions of the wheel took place in a vertical direction, as if the point would throw the former upwards.

That the wheel does not continuously rotate towards the metallic face may be accounted for by the fact that the thin foil very soon acquires the temperature of the sides, since the latter are only warmed by the rays of a thin needle. If the temperature of the sides of the vanes is the same on both faces, no rotation takes place. The metallic face is afterwards, however, more strongly warmed than the mica one, and rotation towards the latter must therefore take place.

After these experiments the supposition appears to me *very probable* that the motion of the vanes towards the aluminum face at the highest rarefaction is a consequence of the *heating* of the glass sides by the kathode rays.

It was also to be expected, from these experiments, that the electrical current at a lower degree of rarefaction, when the glow-light appears, would warm the kathode more strongly than at the highest rarefaction, when phosphorescence is produced. In the first case very probably the detached particles of the electrode strike against the kathode very frequently, and restore part of their motion to it, whereas in the latter case most of the particles strike and warm the glass side.

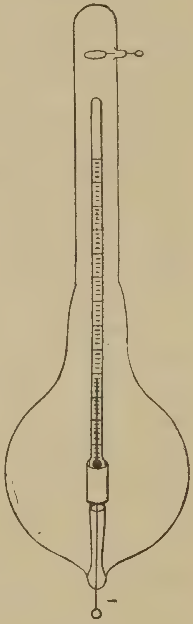
To test this supposition, the temperature of the kathode was measured in a pear-shaped glass vessel at different pressures.

The cylindrical bulb of the thermometer was so closely surrounded with aluminum foil that the discharges could only take place towards the outside (fig. 46, p. 290). The thermometer-bulb was very small, and rested on a small glass tube in the middle of the glass vessel. Experiment showed, as I have predicted, that the temperature of the kathode is greater when immerged in glow-light than when the glass walls surrounding the thermometer-bulb phosphoresce. In the former case the temperature was 47° C., in the latter 41° C., in spite of the smaller thermal conductivity of the rarefied gas. This proves conclusively that the temperature of the kathode decreases if the rarefaction increases.

There are thus two forces principally which cause the motion of the wheel at a high degree of rarefaction :—1, the action of heat on the vanes ; and 2, the action of heat from the surrounding glass side. Each action is opposed to the other ;

the former drives the vanes towards the *mica* or *concave* face in consequence of the reaction of the molecules of gas, and the latter, as in an ordinary radiometer, towards the *metallic* or *convex* face.

Fig. 46.



If the induction-current passes through the radiometer at a pressure of 0·02 mm., the reaction of the particles of gas on the vanes is enfeebled by the thermal action at the glass sides and the motion of the fly-wheel is less rapid; it is much more rapid, on the other hand, when the current is broken, because the whole thermal action comes into force on the vanes.

At a certain degree of rarefaction both actions are in equilibrium, and the motion first commences after breaking the current.

At a still higher rarefaction than 0·02 mm., when the glass sides are phosphorescing vividly, the thermal action of the glass sides preponderates and the rotation of the wheel therefore takes place towards the *convex*, *i. e.* the *metallic* face of the vanes.

The cause of the rotation of the wheel towards the convex face between the pressures 140 and 620 mm. is to be looked for in the fact that the positive or ultimately the negative discharge only takes place at the *corners* of the vanes into the *gaseous space.* The particles of gas charged with statical positive or negative electricity are repelled, and their reaction drives the vanes in the opposite direction and thus towards the *convex* face. It is obvious that a semicylindrical vane acts like a system of four points directed towards the same side. In the second vane the corners are oppositely directed, and act thus in the same direction as the first.

At full atmospheric pressure the discharge at the corners of the vanes does not take place into the gaseous space but on to the glass side, because small sparks strike across. These discharges appear to me to be the cause of the motion of the wheel which takes place towards the concave side of the vanes.

On bringing the palm of the hand near to the glass vessel this discharge is prevented, the electricity again discharges itself into the gaseous space, and the rotation takes place at this pressure also towards the convex face.

Whether the statical charges of the glass sides do not influence the motion of the wheel in one direction or the other I have not been able up to now to ascertain.

I purpose shortly carrying out an exact investigation of the statical charges of the glass vessels, and will only mention here that at an extreme rarefaction *both* ends of the wire are *negatively* and the whole glass vessel positively electrical, and that the neutral point with zero tension lies outside the glass vessel.

Electrical Radiometer with Phosphorescent Vanes.

The fly-wheel of the electrical radiometer represented in fig. 47 (p. 292) consists of two obliquely placed mica plates which are covered on one side with a phosphorescent substance and are suspended free to move by means of a glass cap on a needle-point. An arrangement of copper wire prevents the fly-wheel from falling off when the apparatus is inverted.

Ordinary chalk and some sulphur compounds were used as phosphorescent substances, and of the latter the green phosphorescent calcium sulphide is especially distinguished by the high intensity of its light.

A flat aluminum plate placed above the fly-wheel serves as the negative electrode, and is covered with mica on the face away from the wheel. On the passage of the electrical current a conical bundle of rays proceeds downwards from the negative electrode, causes a vivid phosphorescence of the vanes and sets them in rotary motion, which takes place in the direction of the emission of the electrode particles from the kathode.

Electrical Radiometer with Phosphorescent Disc.

A horizontal mica disc turning on a needle-point is divided into sectors and painted with different phosphorescent substances. An aluminum plate cut through in four quadrants serves as the negative electrode, fig. 48. The individual quadrants are placed obliquely towards the mica plate below and take the form of a screw ; the side of the electrode facing upwards is covered with mica in order that the discharges may only take place downwards.

Fig. 47.

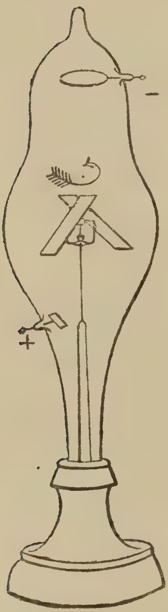


Fig. 48.

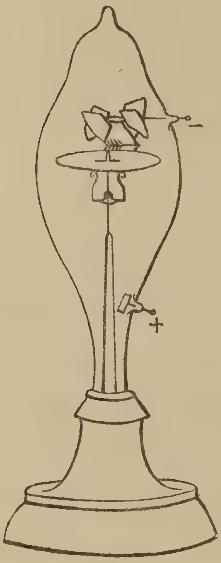
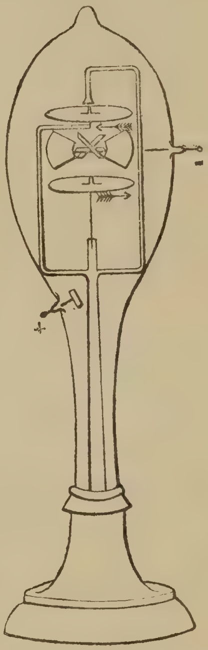


Fig. 49.



At a pressure which is greater than 0·02 mm. the mica disc turns in a direction corresponding to an emission of electrode particles perpendicular to the surface of the kathode, and which we will call a normal rotation. At a greater rarefaction a rotation of the disc takes place in an opposite, abnormal direction, and is to be explained by the fact that the discharges take place principally at the edges of the electrode. In this radiometer an exceedingly rapid rotation of the disc was also noticed when the wires were put to earth, and the radiometer was standing close to the Ruhmkorff apparatus without being in connexion with the poles. The rotation took place sometimes in the one, sometimes in the other direction.

This radiometer shows another remarkable motion. If, namely, the lower electrode, a small plate of aluminum, be used as the kathode, the plate rotates at the greatest rarefaction with a very great velocity in the *normal* direction, thus opposite to the direction of rotation on inversion of the current.

The rays proceeding from the small electrode are distributed almost equally in all directions, and it is therefore inexplicable how *any* motion *at all* of the disc could take place.

The drawing fig. 49 represents an electrical radiometer with two rotating discs; the screw-shaped kathode emits electrode particles against both discs, and causes, at a small rarefaction (0·06 mm.), a rotation in a normal direction. At a greater rarefaction an inversion of the direction of rotation of both discs takes place.

If the lower small electrode be connected to the negative pole of the Ruhmkorff coil, or if the current be inverted, an exceedingly rapid rotation of the lower disc again takes place in a *normal* direction. The rotation of the upper disc is much slower and in the same direction as the lower one, most probably in consequence of the internal friction of the gas, which, as is well known, is still very great even at the highest rarefaction, and in air 50,000 times rarefied scarcely three times smaller than in air of ordinary density.

Phosphorescent Lamp.

A mica lamina covered on one side with green phosphorescent calcium sulphide is fastened obliquely to the vertical in a pear-shaped glass vessel in such a manner that it will be struck by the kathode rays which are emitted from a suitably placed cup-shaped aluminum electrode. Near to the kathode a small plate of aluminum is placed on the side to serve as an anode. Fig. 51 (p. 294) represents the lamp in a somewhat different form. It consists of a simple glass tube having in the centre an obliquely placed elliptical plate of mica covered with sulphide of calcium. Below the mica plate is a disc of aluminum of the same diameter as the section of the tube which serves as the kathode. Above the mica plate is the much smaller anode.

The light of the phosphorescent lamp is sufficiently brilliant to light a room, and it is possible to read even at some distance from it.

The light intermits as often in a second as the primary current is broken; on account of the longer duration of the impression of light, however, the lamp appears continuously luminous, and the intermittent character of the light is only recognized by observing bodies in motion, which then appear multifold.

Some lecture experiments may be introduced here which can be performed by means of the light of the intermittent lamp.

Fig. 50.

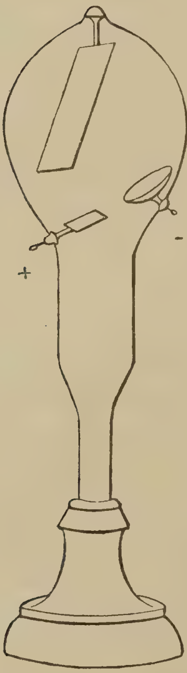
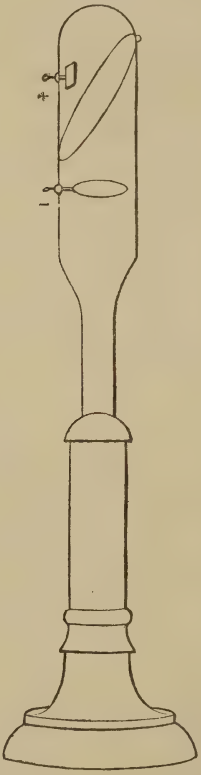


Fig. 51.



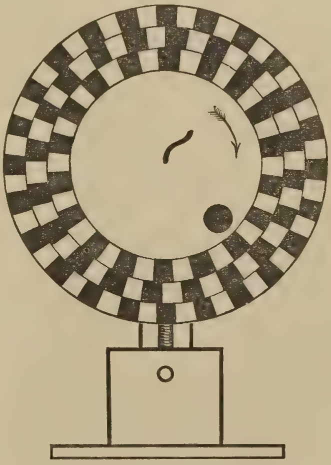
(a) *Experiment with a Mirror.*—If the image of the lamp is looked at in a large mirror which is swung to and fro by means of the hand about a horizontal axis, a whitish elliptical broad streak of light is seen with individual very bright spots of light, the number of which is smaller the quicker the mirror is moved.

(b) *Free fall.*—A large screen of tissue-paper is placed in front of the lamp and separate drops of mercury are allowed to fall in front of it in rapid succession. The paths traversed by the drops appear on the screen in equal times. If an apparently continuous stream of water be illuminated by the lamp, it appears to be resolved into single drops of water.

(c) *Experiment with a Sphere.*—A glass sphere of about 4 cm. diameter is swung on a string in a circle in front of the screen, which is illuminated behind. It appears fourfold if, during the time of its describing a circle, the current is four times broken. The four images of the sphere would always appear at the same place if the velocity of rotation were constant. If the rotation be accelerated, the images are formed at other points of the circle, and the four spheres are seen to advance on account of the longer duration of the impression of light. With a retarded rotation the spheres rotate in the opposite direction. If the sphere be allowed to oscillate about a point as a pendulum, the velocity at different points of the circular path is seen.

(d) *Experiment with the Stroboscopic Disc.*—A disc of cardboard, painted with three concentric circles of black squares, as represented in fig. 52, shows a magnificent optical phenomenon when set in rotation by clockwork andi lluminated by means of the intermittent lamp. Whilst the disc is rotated constantly in one direction, one circle appears to turn in the direction of the hands of a watch, a second in an opposite direction, whereas the third remains apparently at rest; but immediately on altering the velocity of the screen itself, turns in the one or other direction. A curved line drawn radially on the screen, as well as a round black spot, appear to be multiplied, which is to be explained analogously to the several images of the rotating sphere. If the rotating disc

Fig. 52.

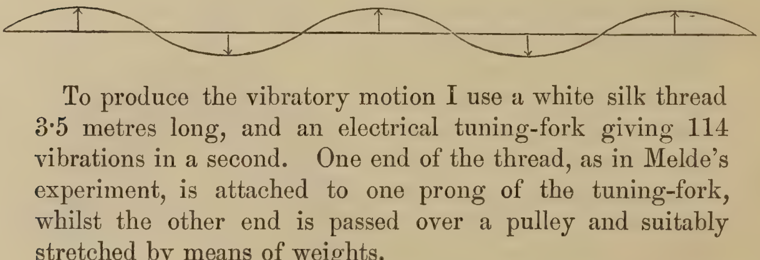


be retarded by means of the finger, a velocity can easily be obtained at which the first, second, or third circle of black squares remains at rest. This manifestly is always the case when a black square comes into the position of the next or of the second or third during the time that the lamp remains dark, because in this case the eye does not observe the motion of the black squares.

(e) *Experiments with Vibrating Wires.*

1. *Objective representation of the true form of a vibrating wire.*—If a wire is vibrating in several segments, separated by nodes, the particles in vibration on opposite sides of a node are, as is well known, in opposite phases of motion, so that the particles of the wire in the one segment move upwards from the position of equilibrium if in the neighbouring segment the motion is downwards. The particles attain their greatest elongation from the position of equilibrium after a quarter of a vibration and the wire forms a wave-line, symmetrical about the position of equilibrium, consisting alternately of elevations and depressions. This curved form of the vibrating wire can be represented objectively by means of the phosphorescent lamp.

Fig. 53.



To produce the vibratory motion I use a white silk thread 3·5 metres long, and an electrical tuning-fork giving 114 vibrations in a second. One end of the thread, as in Melde's experiment, is attached to one prong of the tuning-fork, whilst the other end is passed over a pulley and suitably stretched by means of weights.

If the tuning-fork is vibrating there are formed, as is well-known, *stationary* waves, consisting of several loops whose number varies with the tension of the thread, and is greater the quicker the tuning-fork vibrates, in comparison with the thread, and which are due to the interference of the waves proceeding from the fork and reflected at the pulley, which have equal phases of vibration, but opposite directions of propagation. If the tuning-fork makes n times as many vibrations in a second as the thread would make with its tension and length, the latter divides into n segments, of which each two adjacent ones move in an opposite direction, but vibrate just as quickly as the tuning-fork. The thread which, as a whole, cannot follow the vibrations of the tuning-fork, divides into several subsegments, of such a length that each one vibrates just as quickly as the tuning-fork at the tension existing in the thread. I demonstrate the latter fact in lectures by bringing a strip of stout paper, or a small paper screen, close to a loop. The rhythmical impulses of the vibrating thread give rise to a tone, audible at great distances, of the *same* pitch as that of the tuning-fork.

If now the lamp described became luminous every time that the particles of the thread reached the position represented in fig. 53 of their greatest elongation from the position of equilibrium, an observer must see the wave-like form of the thread at the same place every time. If, moreover, the flashes of light followed one another so quickly that the interval of time between two flashes was equal to the duration of the luminous impression, an observer would see the wave-like form of the thread under an apparently *constant* illumination and always in the same place.

The condition therefore that the experiment shall succeed, is obviously that the vibrations of the tuning-fork and those of the Neef's hammer shall be *isochronous.*

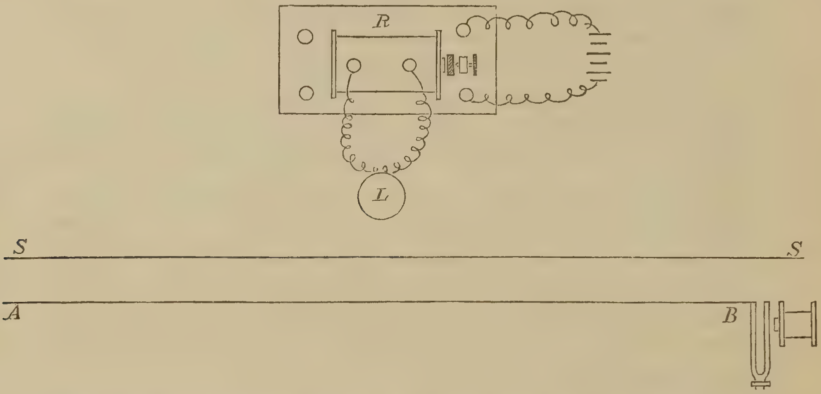
The wave-like form of the thread must, however, also be apparent if the flashes take place after every second, third, or nth vibration of the particles of the thread or of the tuning-fork.

Thus, for example, by using a tuning-fork with 114 vibrations, the wave-line would also be seen if the Neef's hammer were making 19 or 38 vibrations per second. The flashes of light would occur in the first case after every sixth, and in the second after every third, vibration of the tuning-fork.

If the number of vibrations of the Neef's hammer only differs slightly from that of the tuning-fork, which can be brought about at any time by regulating the screw, a slow to and fro vibration of the wave-like form of the thread is observed about the position of equilibrium, *in which each* *vibration of the thread is accompanied by a modulation of the tone.* The particles on both sides of the nodes move in this case always in an opposite direction.

The arrangement of the experiment is diagrammatically represented in fig. 54. AB is the vibrating thread with the electrical tuning-fork; L the phosphorescent lamp which is set in operation by the Ruhmkorff apparatus R, and SS is a screen of tissue-paper.

Fig. 54.

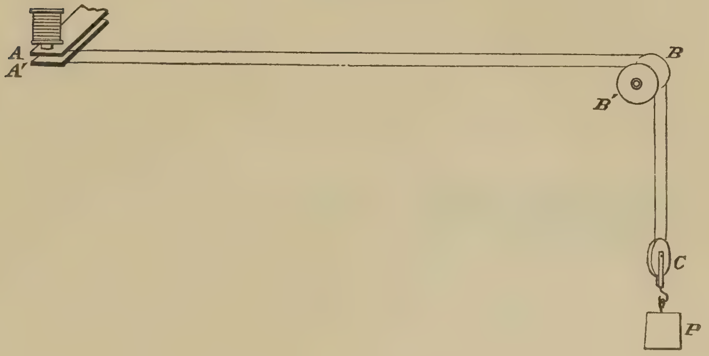


2. *An interference experiment with two vibrating wires.*—Two wave-motions which are propagated in a medium in the same direction destroy each other, as is well known, if the difference in the length of path of both waves is an unequal number of half wave-lengths.

This result of the undulatory theory, which was first of all deduced to explain the acoustical phenomenon that in certain cases two tones can destroy one another, can be proved for *longitudinal* vibrations by means of König's interference-tubes. An analogous experiment in acoustics for *transverse* vibrations has up to the present been wanting, and the chief proof of the undulatory theory of light, which consisted in the fact that if light be added to light under certain conditions darkness ensues, had, critically considered, no perfect analogy in *experimental* acoustics.

To cause interference of transverse vibrations two silk cords, AB and A′B′, 3·5 m. long, equally stretched by means of a movable pulley C and the weight P, as represented in fig. 55, are set in vibration by the two prongs of an electrical tuning-fork.

Fig. 55.



Both silk cords divide into an equal number of ventral segments corresponding to the tension and the length of the cord chosen, as shown in fig. 56. On illuminating both silk cords by means of the phosphorescent lamp

Fig. 56.

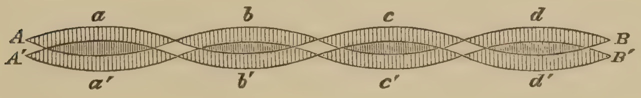
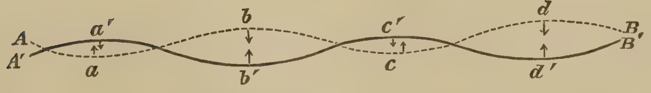
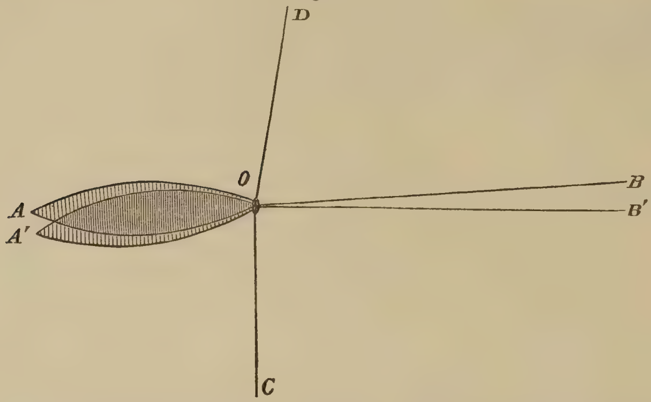


Fig. 57.



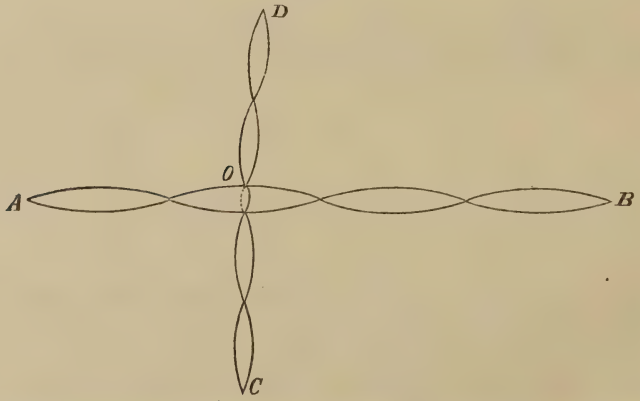
they appear as two wave-vibrations, which differ from one another by half a wave-length, so that an elevation in the one silk cord is opposite to a depression in the second. To cause both wave-vibrations to interfere at any point, it is only necessary to tie a silk thread round two opposite ventral segments, and to draw the loop carefully together. The wave-vibrations proceeding from the two prongs destroy each other in the loop O, fig. 58, and the threads OB and OB′ on the other side of the loop, as well as the two halves of the looped thread OC and OD, remain at rest.

Fig. 58.



On the other hand, the vibratory motion is propagated unaltered through the loop if the latter only contains *one* silk thread, in which case the looped thread vibrates also and divides into several ventral segments separated by nodes (fig. 59).

Fig. 59.



The experiment on interference with two vibrating threads, represented in fig. 58, forms a complete analogy to the interference of two rays of light which mutually destroy one another, as in Fresnel's experiment with the mirror, if the difference in the length of path is equal to half a wave-length, because in this case, as with light, transversal and not longitudinal vibrations are caused to interfere.

Vibrating tuning-forks and plates also, when illuminated by means of the phosphorescent lamp, show similar phenomena to the vibrating wires.

For the lamp, fig. 50, a current giving a 3 to 4 cm. spark is sufficient. A stronger current heats the mica plate, the phosphorescence ceases, and a dark spot appears surrounded by a phosphorescent ring.

For the lamp, fig. 51, a current of 5 to 6 cm. spark-length can be used, because in this case the rays are not concentrated. A stronger current is necessary to heat the mica plate, and therefore with this lamp a luminosity of almost twice the intensity of the first lamp is obtainable.

Action of Approached Conductors on the Electrical Discharges.

If the glass vessel, fig. 50, be touched above the mica plate with the hand or any conductor, or be only breathed upon, the discharges in the lamp are often diminished even to an entire extinction of the phosphorescent light if the current is not too strong. By breathing on the vessel, the discharges are prevented as long as it remains moist. But even the approach of a conductor, too, may considerably enfeeble the discharges.

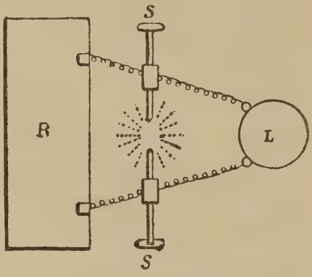
This phenomenon is noticed with the first lamp in yet another way. If the flat aluminum plate is first used as the kathode, in which case the ascending rays strike the whole surface of the mica plate, and the current is afterwards inverted, the mica plate shines at first only faintly but after 3 to 4 seconds suddenly brightens.

If in the second lamp, fig. 51, the mica plate be irradiated first from above and then from below, the spot of light is not only at the commencement very faint, but is *diverted* towards the upper edge of the plate, and suddenly springs after the course of some seconds towards the middle of the plate and becomes brighter.

These and other phenomena of the enfeeblement and cessation of the electrical discharge I endeavoured to explain by supposing *that the statical electricity of the mica plate repels the approaching electricity in the wires.*

If this view were correct, the current electricity must discharge itself at another part of the conductor, where the resistance is less than that in the evacuated space.

Fig. 60.

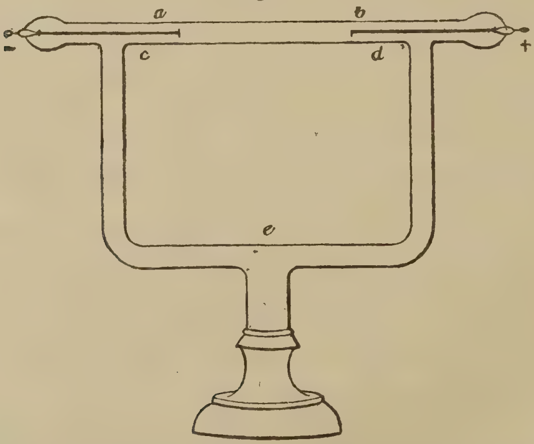


It is therefore only necessary to introduce two discharging points between the two conducting wires, and a striking distance can always be found such that a discharge will take place between the points as soon as the glass vessel is breathed upon or is touched with the hand. The arrangement of the apparatus is represented in the accompanying sketch; R is the Ruhmkorff coil, S the discharging points, and L the lamp.

Apparatus for Demonstrating that Electrical Discharges in a Vacuum are prevented by the Statical Electricity of the Sides.

In order to demonstrate this phenomenon easily, I have constructed an apparatus having the shape of a rectangle, into one side of which two wire electrodes are fused with their ends *ab* at a distance of about 8 cm. from each other.

Fig. 61.



At a rarefaction of about 0·06 mm. pressure the electrical discharges take place along the short distance *a b* and the much longer one *c e d*. But if two fingers be placed about the horizontal limb, close to the ends of the electrode, the electrical discharge ceases between the points and becomes stronger along the layer of air *c e d*, which is almost five times as long.

On touching the vertical limbs at *c* and *d*, the discharge can be repelled into the horizontal limb. It is to be expected that by a corresponding choice of the dimensions of the apparatus and of the pressure, the discharge will *only* take place along the shorter distance *a b*, and on touching the glass side with the hand or with a good conductor, tinfoil for example, it will be driven into the lateral tube, which can also be bent a number of times.

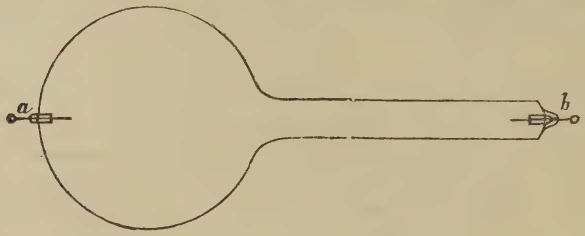
In the London Exhibition of 1868 Prof. Hittorf exhibited a tube which showed a similar case of electrical discharge, and which in my view finds its explanation in the action of statical electricity on the electrodes.

It was a sort of spectrum-tube with a capillary centre piece. The two wide end pieces communicated with each other by means of a side tube twice bent, and were provided with wire electrodes which projected into the capillary part of the tube. The ends of the electrodes were only a few millimetres apart from each other. At a very great rarefaction the electrical discharges did not take place through the shorter distance in the capillary part of the tube, but through the much longer lateral tube.

After what has been said, there can now be no difficulty in explaining this phenomenon. The density of the statical electricity on the sides of the tube will be greater the smaller the section of the tube. Whilst, therefore, the density of the electricity in the capillary centre piece is sufficient to prevent the discharges there, the electrical discharges take place in the *wide* parts of the tube on account of the small density of the electricity of the sides.

That electrical discharges at the highest rarefaction are influenced by the *proximity* of glass sides charged with statical electricity can be demonstrated in an apparatus (fig. 62, p. 304) which we will call an "electrical valve." A wire-shaped electrode *a* is fused into a bulb and a second perfectly similar one (*b*) into a thin tube joined on. At a sufficient rarefaction no current passes when *b* is used as the kathode, whereas after inverting the current, when *a* becomes the kathode, a vivid discharge takes place.

Fig. 62.



It is better to use an influence-machine for these experiments than an inductorium.

After having established these facts it is no longer difficult to explain an experiment which has already been described on p. 255 ; that is, the phenomenon observed in the bulb-tube represented in fig. 5, *that at high degrees of rarefaction the electrical discharge takes place at that point on the kathode which is nearest to the anode,* which, as Mr. Crookes has experimentally determined, is not the case at moderate rarefactions, when the kathode rays are propagated in a straight direction quite independently of the anode. The negative charges of the glass sides will be weaker near to the anode than at all other parts of the glass tube, on account of which the discharge will also take place most easily at that point on the kathode which is nearest to the anode. Thus in the bulb-tube (fig. 5) the kathode discharges itself even in the narrow tube *d* if *a* be used as the positive electrode, whilst the discharge in the bulbs B, C, and D is prevented by the action of the electrified sides.

From my point of view, too, the very interesting phenomenon which I have often observed can be quite easily explained by means of statical electricity, namely that a tube flooded with blue glow-light touched at one point with the finger shows a very bright phosphorescent spot on the opposite side, *as if the point touched were a kathode.* The point in consequence of being touched becomes *strongly negatively electrical* on the inner side, and the particles of the electrode flying past, parallel to the side, are caused to diverge from their straight paths by the statical electricity of the side, and are diverted towards the opposite side, which phosphoresces on being struck by the particles.

The cessation of electrical discharges in strongly evacuated tubes is often put forward as a proof of the unitary view of the nature of electricity. If, as is considered, the electric current consists in the progressive transport of an imponderable matter, the æther, the discharges must continue even in the best vacuum, for æther is still present in it. In opposition to this it may be remarked that electrical discharges take place the more easily at the same degree of rarefaction the further the sides are from the kathode; and after what has been said we are justified in expecting *that electrical discharges would take place even in the best vacuum if the inevitable charges of the adjacent glass sides were not present.*

How are the Statical Charges of the Glass Sides formed?

The statical charges in the neighbourhood of the negative electrode can be formed either by induction due to the kathode, or in consequence of the direct transmission of statical electricity by the particles thrown off from the kathode which are charged with statical negative electricity.

By such an induction the phenomenon is to be explained that bodies which are close to a kathode are no longer repelled at the highest rarefaction by the particles of the electrode which are thrown off, but *are attracted* by the kathode. I often noticed this attraction, even at a small rarefaction, when a mica plate was placed opposite a platinum electrode in order to coat it with a platinum mirror.

In another apparatus an aluminum plate, which served at the same time as the anode, was placed at a distance of about 2 to 3 mm. below the kathode, and the attraction was so strong that the plate was bent round and was united with the kathode.

The statical electricity is, however, also *directly* transmitted to the walls, since, according to the view advanced and verified in many cases by me as to the nature of radiant electrode matter, very small solid particles, charged with negative electricity, are torn off and thrown from the kathode and give up for the most part their negative electricity to the surrounding sides. The negative electricity of the inner glass sides attracts the positive electricity of the outer sides, whilst the negative electricity of the latter is given up to the external air.

The evacuated glass vessel thus forms a sort of Leyden jar with an internal negative and an external positive charge, which often, especially at the highest rarefaction, are so strong that the thin glass sides are perforated. As I have already mentioned in another place, the external charge of a glass vessel is positive at the highest rarefaction, whereas the kathode, as well as the anode wire, are negatively electrical. The glass apparatus was tested as to its electrical charges by means of an insulated copper wire, which was first of all made to touch at different points of the glass side, and then brought into connexion with the conducting wire of a very delicate quadrant electrometer. It was shown thereby that the density of the statical electricity was at its maximum opposite the points of discharge of the kathode.

I may mention further in connexion with this that strongly evacuated glass tubes, and vessels like a Leyden jar, require a longer time in order to become *charged* with statical electricity, and that they only discharge in the interior after reaching a definite potential. This gradual charge and sudden discharge can be very beautifully observed with the phosphorescent lamp (fig. 51, p. 295), if it be connected with the conductors of a Töppler's machine. On turning the machine slowly the lamp continues dark for some time, and becomes suddenly very bright as soon as the discharge takes place in the interior. The flashes of light take place more quickly the faster the machine is turned.

Electrical Phenomena in the Celestial Vacuum.

How far the so-called vacuum, which we can obtain with the best means at our disposal, is removed from an absolutely empty space has been shown by the experiments on internal friction, which Kundt and I have carried out in extremely rarefied gases*. In air at a pressure of 0·03 mm. of mercury the internal friction, and thus also the conduction for heat proportional to it, is scarcely three times smaller than in air of ordinary density. In air rarefied more than 25,000 times, very considerable quantities of motion can be transmitted from place to place by means of internal friction of the mass of air ; for example, a horizontally rotating mica plate sets in motion a second one parallel to it even at great distances. We conclude from this that the mass of gas in an artificial vacuum must be still relatively very large, even at a million-fold rarefaction ; according to the calculation of the kinetic theory of gases, a cubic centimetre would still contain about 21×10^{12} molecules of air, which move to and fro between a number of inconceivably small atoms of æther.

We are quite as little justified according to the present state of our knowledge in assuming cosmical space to be void any more than the artificial vacuum. Light and heat radiation furnish, as is well known, a certain proof that the interstellar space is filled with a very attenuated matter which the older philosophers called æther †. Further, by exact measurements and calculations of the astronomers, a constant decrease of the long axis of the path of Encke's comet has been proved, and this decrease in the path of the comet has been ascribed to the retarding action of attenuated matter. It is, however, still an open question whether the retarding medium is identical with the æther or is peculiar to each solar system, and, like the atmosphere about Herschel's nebulæ, surrounds it to a certain distance ; so much is, however, certain, that the vacuum of the universe, too, is not absolutely void. If, now, a space filled with æther conducts electricity, it is easily explained how electrical disturbances of equilibrium on one heavenly body must cause the same on all neighbouring ones. Thus, along with gravitation, light, and heat radiation, electricity will also belong to those forces of nature which connect distant heavenly bodies with one another.

It will scarcely be doubted by any one that the northern and southern lights, which appear almost uninterruptedly in the higher* regions of our atmosphere in the neighbourhood of the poles, attaining sometimes an intensity of light equal to that of the first quarter of the moon, and are even visible in sunshine by their vibrations of light, are ascending electrical discharges. Opinions, however, differ as to the cause of this luminous phenomenon.

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* Poggendorff's *Annalen*, clv.; *Sitzungsberichte der k. Akademie der Wissenschaft*, lxxviii.

† In Sanskrit *âschtra* = air circle and the root *as, asch* denotes to shine.

De la Rive considers this luminous process as a recombination of the positive electricity of the air with the negative electricity of the earth, which have been separated directly or indirectly by the heat of the sun in the equatorial regions. Why, however, the electrical charges do not combine earlier and only in the polar regions is not apparent, more especially as air is a bad conductor of electricity. If, however, the vacuum of the universe conducts electricity, the supposition lies very close that the polar light is of *cosmical* origin †, and is especially caused by electrical disturbances on the solar surface. Sun and earth form as it were two mighty electrodes in the universe, between which electrical discharges take place through the vacuum. The dependence of the intensity of the phenomenon on the size of the sun-spots also points to a cosmical origin, as was lately observed in the Kew Observatory from April 15–21, when very vivid auroræ boreales appeared in America. The maximum intensity of the aurora was attained on April 17, when the sun's disc showed an extraordinarily large sun-spot.

It is not improbable that such a luminous process takes place on other planets, and certainly Venus often shows a phosphorescent light on the side not illuminated by the sun. Sheet lightning, too, is undoubtedly an electrical discharge in a rarefied atmosphere, which often continues in calm air between the clouds for hours, and so also, most probably, is that luminosity of large clouds without flickering observed by Rozier and Beccaria, as well as the luminosity of dry mist, as in the years 1783 and 1831 ‡. The observation, too, has often been made that at the time of the aurora borealis dark parts of the heavens shine brightly owing to falling stars. This and still another circumstance, viz., that, after the disappearance of many shooting stars and meteorites, phosphorescent nebular formations remain visible for a long time, render the supposition probable that the luminous phenomena of meteors and meteorites are caused, not only by the incandescence of the outside layer of the moving body, but also by the surrounding gas-masses becoming electrical. Admiral Krusenstein, in his voyage round the world, saw for an hour together the tail of a meteorite which had long disappeared. A similar spectacle was presented by the meteorite of 1873, which commenced to shine 22 miles above the surface of the earth south of Raab, moved over Lower Austria, Moravia, and Bohemia, and became extinguished near Zittau, at a height of 4·5 miles. The intensely white zigzag tail of this meteor was visible for half an hour afterwards. The long duration of the luminosity is not explicable on the assumption that the tail consists of glowing gases, especially if we consider that the loss of heat of bodies in a vacuum by radiation is relatively large, even with a small difference of temperature in the surrounding medium, and must be much greater in cosmical space, the temperature of which, according to Pouillet's actinometric measurements, is said to be −142° C. Even large pieces of carbon, as I have noticed, sink almost momentarily from a white to a red heat in very rarefied air. On the other hand, the energy of the progressive motion can just as well be converted into electricity as into heat, and therefore the assumption is justified that meteors represent an electrical and at the same time a glow-light phenomenon.

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* Newton finds by observations of 26 auroræ boreales that the height of these phenomena varies between 33 and 281 English miles above the surface of the earth.—Nature, xxii., p. 291, 1880.

† Edlund, Wiedemann's *Annalen*, 1882, p. 514.

‡ Humboldt's *Kosmos*, 1874, vol. i. p. 127.

The tails of comets, too, which extend over many million miles are formed, according to Zöllner's view, by electrical processes which are caused by the action of the sun. If a comet, which is said to be a formation of fluid meteor masses, comes near to the sun, evaporating and boiling processes take place on the side turned towards it, and a vapour mantle is formed, and at the same time, also, electricity is continuously given off. The formation of the tail of the comet in a direction away from the sun is explicable by the repulsion between the electrical solar atmosphere and the electricity of the same kind in the vapour envelope. If the electricity of the vapour envelope of the comet should, for any reason, become of opposite sign, the tail must be turned towards the sun, which is also sometimes noticed. This ingenious theory, which Zöllner has applied to the individual phenomena which had hitherto been observed in comets, such as curvature of the tail, oscillatory motion of the efflux, multiplication of the vapour envelopes, &c., promises more success than all other hypotheses which have been advanced in this problematical sphere.

Conclusions from the Experiments.

Starting from the unitary view as to the nature of electricity, I have explained the phosphorescent actions of radiant electrode matter in the following manner. The extremely attenuated matter the æther, which fills the whole universe and transmits light and heat, surrounds the atoms and molecules of a body just as the atmosphere surrounds the earth. In the normal condition each body has a definite quantity of this continually moving matter. If it possesses more æther than it should have corresponding to the density of the same in our part of the universe, then it is positively electrical; on the other hand, negatively electrical when it contains less æther. Now, if the negatively electrical particles of the electrode strike the glass, then, besides the agitation of the corporeal molecules, there will be an equalization of the quantities of æther between the striking particles and the part struck, which equalization cannot take place without an agitation of the æther envelopes of the molecules. Each spot of the glass struck becomes the centre of waves of æther quite analogous to a calm surface of water, which, when struck by drops of rain, shows waves of water in the plane. In consequence of these waves of æther thus sent into the exhausted space the glass side becomes luminous with a phosphorescent light peculiar to it, which is different according to the composition of the glass, because the wave-motion, in consequence of the difference of the density of the æther, will also be different.

That, in the impact, part of the energy of the progressive motion of the infinitely small projectiles of electrode matter is changed into vibratory motion of the molecules of the glass, that is into *heat*, is just as self-evident as the conversion of that energy into progressive motion of the movable fly-wheel which is struck by particles of the electrode.

I have further succeeded in completely explaining the action of a magnet on the kathode rays by means of *molecular electrical convection*, and in bringing under *one* point of view this phenomenon, as well as Plücker's "magnetic surfaces," Hittorf's spiral-like convolutions of the glow-light, and the triple surfaces observed by Reitlinger and Urbanitzky.

The complete agreement of the theoretical results of molecular electrical convection with all the phenomena which have up to the present been observed, justifies the conclusion that the assumption as to the nature of radiant electrode matter, which serves as the starting-point of that explanation, is correct.

According to the dualistic view it is supposed that, in a conductor transmitting an electrical current, two equal quantities of dissimilar electricities are flowing in opposite directions. From Rowland's experiments on the transport of electricity by conductors and the views advanced in this communication on molecular electrical convection, it follows that even the motion of *a single* electricity in the sense of the unitary hypothesis exerts the same action on a magnetic needle as an electrical current flowing in a conductor at rest. But what appears to speak especially for the unitary view is the fact, which has long been known, that the electrical current only detaches particles *mechanically* from *one* pole.

If, for instance, we wish to assume that only that motion which manifests itself as negative electricity can separate the particles, we find another fact, that the current from the positive pole can detach the particles, as is the case with the electrical arc-lamp, in which the particles are transferred from the positive to the negative carbon point.

On the supposition that the electrical current is a real flowing of the æther, the facts alluded to can be easily explained.

I will here meet an objection which might possibly be raised against the æther theory of the electrical current, viz. that the mechanical action of the latter can be considerable, whilst the mass of the æther is infinitely small. According to the calculation of Mr. P. Glan, the æther in a certain space (*e.g.* 1 c.c.) has very probably more mass than the hundred billionth part of the same space if it were filled with hydrogen of normal density. The highest limiting value given by Sir W. Thomson for the density of the æther is 7400 times larger[*].

The mechanical action of masses in motion depends upon the *vis viva*—mv^2; it is greater the greater the mass or the square of the velocity of motion. We could thus explain the great mechanical actions of the electrical current, either by the great velocity of a small mass of moving æther, or, conversely, by a large mass of æther moving at a small velocity. The latter, however, appears to be the case, and the mechanical disruption of a particle of the electrode by the electrical current would thus be owing to the transference of a very large quantity of æther, which flows through the conductor with a small velocity.

It may further be remarked here that Wheatstone's experiments on the non-simultaneity of the sparks at different breaks in the circuit do not give any solution as to the *velocity of the current.* On the æther theory of the electrical current these experiments would only show that an excess or deficiency of æther, a condensation or rarefaction of the same, which is formed at one point of the conductor, is transferred at a very high velocity. It was, *à priori,* to be expected from the wave-theory that this velocity "*of the diffusion of the current,*" as W. Weber[†] calls it, would be of the same order as the velocity of the propagation of light; and this is confirmed by Wheatstone's[‡] experiment.

Whilst the *velocity of propagation of motion* from particle to particle is very great, the special motion of these particles—the *current velocity*—is very small, and is, according to Weber, 0·5 millim. in a second for a moist conductor (water).

Weber finds that in a current the intensity of which, according to *electrolytic* measurement, is $= 1$, a quantity of positive electricity equal to $106\frac{2}{3} \times 155370 \times 10^6$ units passes in one second in one direction through the section of the conductor, in conjunction with $\frac{1}{9}$ mgm. of hydrogen, and an equal amount of negative electricity in the opposite direction together with $\frac{8}{9}$ mgm. of oxygen.

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[*] Wiedemann's *Annalen,* vii. p. 658.

[†] *Electrodynamische Maassbestimmungen,* Abhandl. 2, p. 299.

[‡] Ditto. Treatise 4, p. 281.

Hence it follows that $106\frac{2}{3} \times 155370 \times 10^6$ units of positive and just as many of negative electricity must be contained in 1 mgm. of water; these, however, only progress, together with their ponderable carriers, with the velocity alluded to (0·5 mm. in a second) if the section of the moist conductor is only a square millimetre.

On this supposition it can no longer appear strange that an exceedingly attenuated matter like the æther can, nevertheless, cause an extremely violent action, which can put incomparably larger molecules of a body into a motion of heat, and even detach them from the body and throw them off with a very considerable velocity. It is evident, from the nature of the case, that this detachment of particles will only take place at the point where the current is emitted, which, however, does not imply that at the opposite pole, in consequence of another cause—possibly strong heating—detachment of ponderable matter could not take place.

Besides this the particles of æther will rub against one another in the spaces between the molecules of ponderable matter, and transmit part of the energy of their motion to the molecules of the body, causing in the latter vibratory motions like the vibrations of the strings of an æolian harp by the progressive motion of currents of air.

If we wished to draw conclusions as to the direction of the hypothetical æther current from the direction of motion of the detached particles of the electrode, we must suppose that in induction-currents in rarefied spaces it proceeds from the *negative* to the *positive* pole; on the other hand, in galvanic currents in the *opposite* direction, because in the latter a transference of the detached particles takes place from the positive to the negative pole, when the electrodes are of the same metal and of approximately equal shape.

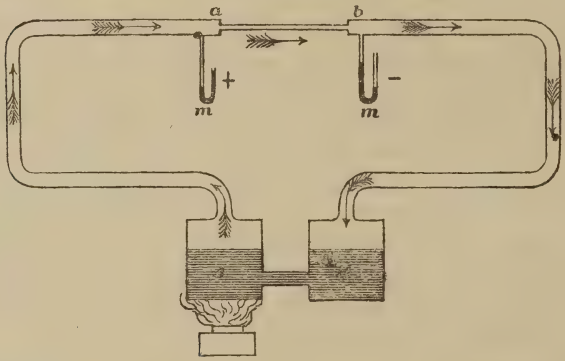
Resting on these two facts, we have at the point of emission of the galvanic current free positive and of the induction-current free negative tension.

We can therefore put the following question: Can an inversion of the tensions take place at the point where the æther current is emitted, and what is the cause of it?

The explanation is given without recourse to any hypothesis, simply from the well-known laws of convection, which have been experimentally proved, which all fluids must follow and therefore the æther also.

These laws may be elucidated first with a ponderable fluid, for example superheated steam. Fig. 63 represents a system of tubes, which is in connexion with two communicating vessels filled with water. Steam is generated in A and superheated; it flows through a system of tubes, into which a capillary *a b* is introduced, and which is provided with two open manometers, *m*, and condenses in B.

Fig. 63.



It is easily seen that the manometer at *a* will show a packing, and at *b* a rarefaction of the steam. The excess of steam shall be represented by +, and the deficit by —.

If a vessel of greater section than that of the conducting tubes be introduced instead of the capillary, a rarefaction (—) will be formed at the point of emergence from, and a compression (+) at the point of entrance into, the system of tubes.

The current of æther continuously generated in a battery by chemical forces will in a manner quite analogous be compressed by the greater resistance on its entrance into a conductor, and on its exit from it will be rarefied. At the former point an excess, at the latter a deficiency, of æther or positive and negative free tension will be produced. This condition of things takes place in the electrical arc-lamp, in which the distance of air between the carbon points offers a considerable resistance to the galvanic current.

The layer of air in evacuated tubes is certainly much greater in comparison to the distance of air between the carbon points, but the tension of induction-currents also is far greater than that of galvanic currents. The layer of air in the evacuated tube offers a small resistance to the induction-current, and therefore the negative pole is at the point of entrance into the layer of air.

This explanation of the inversion of the tensions of electricity certainly in simplicity leaves scarcely anything to be wished for, and the analogy between the phenomena of the convection of liquids and those of the electrical current is so great that it would not be easily possible to overlook it. I do not know also how the fact of the inversion of the poles could be better and more simply explained according to the now dominant dualistic theory.

Another conclusion can be drawn from the hypothesis advanced as to the nature of the electrical current which is in best accordance with observation. If a battery is closed by a wire, it opposes a resistance to the æther which is striving to equalize itself, and therefore a partial packing of the æther occurs in the wire which, beginning at the positive pole, decreases towards the middle of the wire up to a point at which the free tension is zero. On the other side of this boundary a deficiency of æther, that is negative free tension, manifests itself in a continuously increasing manner quite analogous to the fall in pressure in flowing liquids. Whilst this distribution of free tensions in the conducting wire is self-evident according to the æther theory, the prevalent dualistic theory offers no answer to the question why the free electricities in the conducting wire do not combine with one another as they otherwise do in an extraordinarily short space of time.

On the other hand, it is evident that the case will also be the same in evacuated tubes. A deficiency of æther, that is a negative free tension, is formed at the point where the current of æther enters the column of gas, whereas at the positive pole an accumulation of the æther, positive free tension, occurs. There must, therefore, be one point between both poles which would act neither positively nor negatively towards other bodies, and this *indifferent* place would fit very well for the *dark space* between the positive brush of light and the glow-light*.

The facts proved by direct experiment by De la Rive verify this assumption, viz.: that the dark space is *colder* than the rest of the path of discharge, and that a distinctive *flowing of electricity cannot be detected* in it†.

The above assumption is also in best agreement with the results of the electroscopic investigations of evacuated tubes which are traversed by an induction-current.

If a tube traversed by an induction-current and insulated at both electrodes be connected to an electroscope by means of a strip of tin-foil and tested at various points, it will be found, as Prof. G. Wiedemann has proved, that the tube is negatively electrical in the neighbourhood of the negative, and positively electrical in the neighbourhood of the positive pole. Both electrical free tensions decrease towards the dark space, and are here almost zero. The small tension of the glass tube about the dark space is sufficiently explained on the assumption that the propagation of electricity also takes place through the glass, and that in this conductor the indifferent zone can occur at a different point to that in the inner column of gas. This can be verified by charging only one electrode, the other being put to earth. The tube appears indifferent at the emergent electrode, and is in its whole length similarly electrical to the charged electrode‡.

If the explanation of the dark space given is correct, the stratified structure of the positive brush-light can be explained as follows. It is probable that the dark space is only the first dark stratum, and that all dark parts in the positive brush of light are just as many indifferent points or strata of no tension, the origin of which could be explained mechanically. The intermittent discharges of the particles detached from the electrode will cause compressions and rarefactions in the enclosed column of air, which will take place the more regularly, the more regular is the vibration of the contact-breaker. The number of these waves will depend upon the nature of the gas and the form of the vessel and of the electrodes.

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* As distinguished from the dark space immediately at the negative electrode.

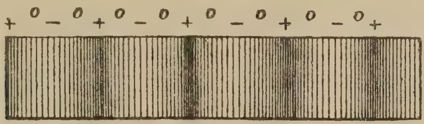
† Poggendorff's *Annalen*, clviii. p. 271.

‡ Poggendorff's *Annalen, tom. cit.* p. 59.

Since, moreover, the rarefied gas offers a smaller resistance to the discharges than the compressed one does, positive and negative tensions will be formed at the points of ingress to and egress from the compressions.

At the points of greatest compression and of greatest rarefaction, free positive and negative tensions will respectively result, as represented in the drawing (fig. 64). The indifferent places (0) will lie between them.

Fig. 64.



That the blue colour of the glow-light does not appear alternately in the strata is to be explained by the fact that the particles of the electrode are here wanting. I only noticed once a very distinct blue surface about 1 millim. thick of the *first* bright whitish stratum on the side facing the negative electrode. Ciamician, who lately has experimented much with spectrum tubes, is said to have also seen such superficial blue-coloured strata.

The compressions and rarefactions of the column of air will certainly be formed throughout the whole tube if the gas is everywhere in an equal state of motion. That this formation of strata in the glow-light must be modified by the electrode particles being violently thrown about, is to be expected.

In the same way no formation of stratification is to be expected with a constant discharge of the electrical current.

If the tube be more strongly exhausted the wave-lengths must increase, but at the same time the number of waves decrease because the glow-light extends further the smaller the resistance to the motion of the residual gas. If the glow-light be repelled by means of a magnet in the neighbourhood of the negative electrode, the strata can be formed in the space free of glow-light. The strata disappear entirely if the glow-light extends to the positive electrode.

Many investigators have been occupied with the explanation of the formation of strata; it would, however, exceed the limits of this communication were I to submit to a criticism the views hitherto advanced on this subject.

As far as I can survey the wide field of the conduction of electricity in rarefied gases, I cannot put aside my conviction that only the assumption of a single movable fluid can explain in an unconstrained manner those electrical phenomena which have hitherto remained an unsolved riddle for the dualistic theory. And if, perhaps, the explanation given may appear very simple, it is, on the other hand, clear and free from new hypotheses and mysticisms.

The æther theory of electricity has become, especially in the last ten years, the subject of a deeper study. Franklin, as is already well known, tried to explain the electrical phenomena known at his time on the assumption of a single electrical fluid. He did not, however, succeed in accounting for the repulsion of two negatively electrical bodies, and Franklin's view and that of the "Unitaries" had to give place to that of the "Dualists," who would explain the electrical phenomena with two electricities. Only latterly has the unitary idea been again taken up by important scientific men, and further extended with success.

I must here, first of all, refer to a meritorious man, the astronomer Angelo Secchi, who, in the year 1863 in his book 'The Unity of the Forces of Nature,' clearly expressed the idea that the electrical current is an actual flowing of the æther, and explained, with the help of the experimentally proved laws of hydrodynamics hitherto known, most of the electrostatic and electrodynamic phenomena in a simple and intelligible manner.

Edlund, 1871*, afterwards starting from the assumption of a single fluid, has deduced the empirical formulæ given by Ampère for the mutual action of two elements of current which govern the laws of all electrodynamic phenomena. He relies thereby upon two fundamental principles, viz.:—

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* Poggendorff's *Annalen*, Suppl. vol. vi. pp. 95, 241.

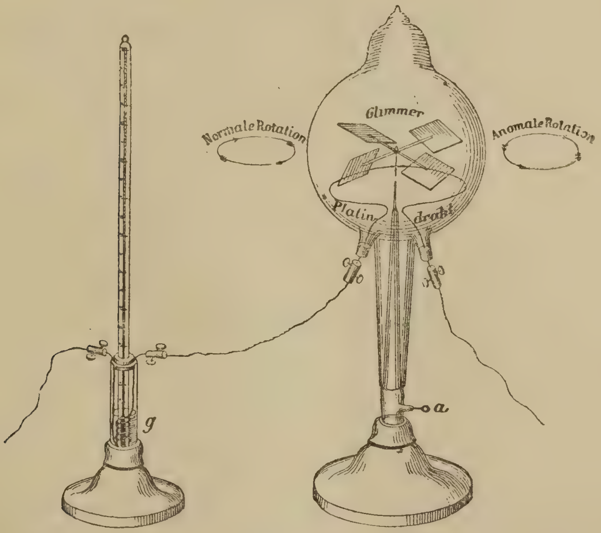
1. On the principle of Archimedes, the application of which to phenomena of this kind appears to be incontestable, and has been verified experimentally by the diamagnetic experiments of Plücker. 2. On the principle that everything which takes place or happens in external nature requires a certain time. Besides this Edlund succeeded in accounting for most of the phenomena of the galvanic current by the æther theory.

Though I cannot disguise to myself the conviction that the æther theory has only few and timorous supporters, I thought that publicity ought to be given, not only to the experimental results of my investigations on radiant electrode matter, but also to the conclusions which I infer from them.

Contribution to the Explanation of Zöllner's Radiometer.

F. Zöllner describes, in the third communication of his *Untersuchungen über die Bewegung strahlender und bestrahlter Körper*,* an ingeniously constructed radiometer, the wonderful phenomena of motion of which have not hitherto been

Fig. 65.



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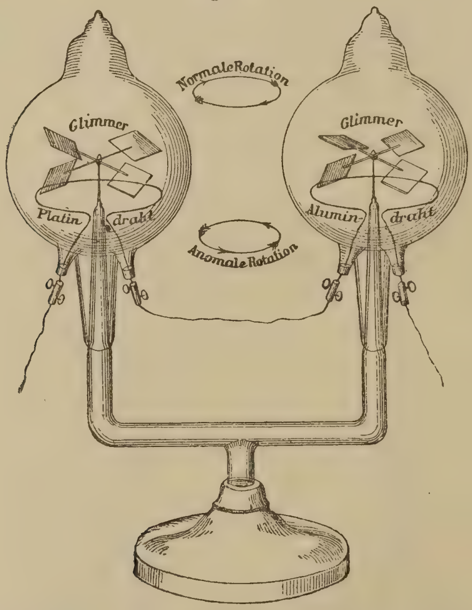
* Poggendorff's *Annalen*, clx. p. 460.

explained. The apparatus consists of a movable cross with unblackened mica plates which, as represented in fig. 65, are obliquely inclined to the horizon. Below the cross is a ring of platinum wire lying horizontally, and its ends fused into the glass in order to transmit a galvanic current.

The rise in temperature of the platinum wire was approximately determined by a thermometer, *g*, which was divided into fifths of a degree, the bulb being surrounded by a platinum wire of the same thickness as that in the radiometer, in a closely-fitting spiral of several turns. The thermometer was then placed in a vessel containing a non-conducting liquid, such as copal varnish, which surrounded the spiral of wire (fig. 65).

The following phenomena were observed in an apparatus with two communicating radiometer-bulbs (fig. 66), which were provided with an aluminum and a platinum ring respectively, with a galvanic rise of temperature of the wire of at most 10° C., and at different pressures of the gas in the interior of the bulbs.

Fig. 66.



1. At an ordinary barometric pressure of 760 mm. a

normal rotation took place, that is, such as could be explained by a heated current of air ascending from the wire.

2. On a continuous decrease of the pressure a turning-point occurred at about 100 mm., when the rotation decreased at this pressure with diminishing velocity to a standstill.

3. At lower pressures than 10 mm. an *abnormal* rotation in the *opposite* direction took place, that is, such a one as could be explained by an *absorption of gas* by the heated wires both of aluminum and of platinum.

4. This abnormal rotation remained unchanged down to pressures which could no longer be determined barometrically, and at which, as it *appeared*, an ordinary radiometer placed simultaneously in connexion with the pump had already passed the point of its greatest sensitiveness.

5. On continued rarefaction the normal rotation again commenced *almost* suddenly, but with such a velocity that it was no longer possible to distinguish the individual parts of the rotating cross. Zöllner had never observed a velocity of rotation even approaching this with the most delicate radiometers when exposed to a most powerful solar radiation. The galvanic heating of the wire need only be 2 to 3°. The turning-point seems to occur approximately simultaneously with the platinum and aluminum wires.

It is self-evident that all these experiments succeed as well when the rings are placed *above* instead of *below* the movable cross, only the direction of rotation is always reversed.

If the vessel be fused off with the enclosed gases at this small pressure, a normal rotation similarly takes place under the same conditions on the galvanic heating of the wires. The velocity of rotation decreases, however, continually until after 8 to 10 days; a stoppage occurs even on heating to a red heat, which is changed later into an abnormal rotation, and these changes can only be caused by a gradual increase of pressure in the interior of the vessel.

Still another experiment which Prof. Zöllner has made is interesting, by simply placing the radiometer in full sunlight. A *normal* rotation took place even if the pressure had so far increased that on galvanic heating of the wire an *abnormal* rotation occurred.

Prof. Zöllner deduced from these experiments that the galvanic current acts on the mica plate not only by the heating caused by it in the wire, but that a specific action on the surrounding gaseous medium must be ascribed to the current, which is of opposite action to that caused by the rise in temperature. This action *could*, according to Zöllner, be explained by a resorption of the surrounding gas.

The following observation is advanced in support of the existence of such a process of absorption. The double apparatus represented in fig. 66 was placed between the double windows of a room after having been closed at a rarefaction corresponding to a *normal* rotation. Whereas for some days after closing a decrease in the normal velocity of rotation had commenced, a slow rotation in the abnormal direction was noticed one evening in the moonlight. This rotation was also noticed at night without moonlight during a period of time of four weeks. By day, too, with a thickly covered sky the same rotation took place, whereas rest occurred on bright illumination, which on irradiation by the sun was transformed into a *normal* rotation. It lost, however, this property by degrees.

Another fact is shortly alluded to in the paper. Prof. Zöllner surmised that the phenomenon was in connexion with an irradiation towards space, and opened therefore the outer window in order to increase this emission of rays, whilst the inner one was closed again. The action which took place was opposite to that expected ; the motion ceased completely after the expiration of half a minute. As soon, however, as the outer window was closed again the abnormal rotation recommenced. Zöllner often repeated this experiment with equal success, and showed it to his friends.

During a lecture I was giving to a scientific society on "Radiant Electrode Matter," I noticed that the wheel in a Zöllner's radiometer of the form represented in fig. 65 turned in an *abnormal* direction at a degree of rarefaction at which *normal* rotation took place in consequence of galvanic heating or of emission of radiant electrode matter, for which purpose another electrode was fused into the radiometer at *a*, fig. 65. I thought at once of the moonlight in Zöllner's experiment, and it appeared to me very probable that the cause of this problematical motion might be due to the radiation from a series of gas-burners, which were placed at a distance of about 3 metres from the lecture-table, almost at the ceiling, in the lecture-hall.

I surmised that an illumination of the radiometer from below would cause a motion in the opposite direction. The experiment was afterwards tried with a batswing burner, and my supposition verified. If the flame was vertically or obliquely above the apparatus, the rotation took place in an *abnormal* direction and was changed into an oppositely *normal* direction if the flame was placed below the apparatus.

If, further, the vessel of the apparatus was covered with blotting-paper soaked with ether and was still warmed below the cross by touching with the hand, a very rapid rotation took place in an *abnormal* direction. An opposite rotation took place on cooling the lower and heating the upper part of the glass vessel.

On one forenoon I noticed with the same apparatus a rotation in an *abnormal* direction, although no sun's rays penetrated into the room, and the apparatus only stood in diffused light in the neighbourhood of the window. In the afternoon it came to rest.

It might have been conjectured that the cause of this motion was the radiation from the ceiling of the room, which was relatively warmer than the ground in the forenoon than in the afternoon.

I made an experiment with hot copper plates, which I placed horizontally at a distance of about a metre above and below the radiometer. The result showed that heat and light rays cause the *same* rotation, an *abnormal* by irradiation of the vessel from above, and a *normal* by irradiation from below.

I repeated also Zöllner's experiment by placing the radiometer directly in the sunlight. The cross revolved in a *normal* direction. However, on allowing a pencil of solar rays, which entered the workroom through a hole of about 7 cm. diameter, to fall on the radiometer from above, the cross rotated in an *abnormal* direction as with the gas-light and heat-rays, and returned to the *normal* direction as soon as the pencil of rays was turned on to the lower part of the apparatus by means of a mirror.

These, as well as the radiometric experiments made by

Prof. Zöllner at a greater rarefaction (0·02 millim. mercury pressure), can be explained in the following way:—

If the hot metallic plate, PP (fig. 67), be placed above the spherically-shaped apparatus, only the upper half of it is struck by heat-rays and heated. The sketch represents a section of the glass vessel in the vertical plane tangential to the platinum ring; *r r* is a piece of the platinum ring, and *m m* the section of the mica plate placed obliquely to that vertical plane.

The molecules of gas striking against the upper glass side leave it with a greater velocity, and convey by collisions a part of their kinetic energy to the vanes, *m m*, which, in consequence, will experience an excess of pressure normal to the surface. The vertical component of this pressure is neutralized by the point, whereas the second component parallel to the ring drives the vane in an *abnormal* direction, as is apparent from the sketch.

It is easily seen that, if the plate be placed below the apparatus, the small plates will experience an excess of pressure from below to above directed normally against the surface, and that therefore the motion must be reversed.

Fig. 67.

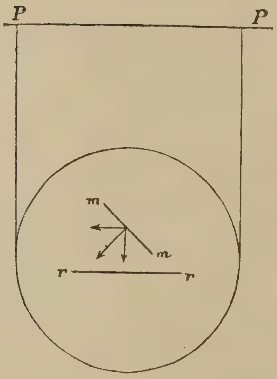
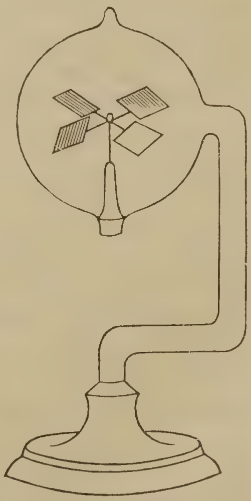


Fig. 68.



From this follows the following explanation for Zöllner's experiment by moonlight. The motion is caused partially by the faint moonlight, but *principally* by *heat* which is emitted from the upper part of the double window more strongly than from the lower. With an open window the temperature has become equalized in the whole space of the double window, and a stoppage takes place in the motion. The stronger radiation of heat from *above* was the cause of the *abnormal* motion which was noticed by Prof. Zöllner also *without* moonlight and by me in the forenoon in a warmed room. In the afternoon the temperature had become equalized, and the small difference of temperature between the ceiling and the floor was not sufficient to overcome the resistances to motion. The wire ring is of secondary importance for this experiment; it will weaken or strengthen the motion according to whether the irradiation takes place from above or below. That these experiments must succeed also without the wire ring follows from the explanation given. I have made experiments of this kind with success, and indeed with the apparatus represented in fig. 68.

The cross rotates in an abnormal or normal direction, according as it is warmed by the hand either above or below.

If the apparatus be acted upon by luminous rays, and in such a manner that they fall upon it from above, the rays of light will pass through the glass sides and strike the upper surfaces of the mica plates, and since the latter conduct heat badly they will be warmer on the irradiated side than on that which is in shade. Hence from the reaction of the gas molecules there results a pressure directed perpendicular to the plates and downwards, which turns the plates in an abnormal direction. On illuminating the apparatus from below, the conditions and direction of rotation are reversed.

If the apparatus *without a wire ring* be placed in full sunlight, both actions are more or less in equilibrium, and even if the radiation from above be somewhat stronger, this small difference in the radiation is not sufficient to overcome the resistances to motion; such an apparatus must therefore *remain at rest* in full sunlight.

Prof. Zöllner has already made this experiment*. In the first communication of his investigations, in reference to an apparatus in which a disc of aluminum foil was placed below the cross instead of the platinum ring, he remarks as follows:

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* Pogg. *Annalen*, clx. p. 166.

"The cross just described shows, when enclosed by itself in a glass vessel in the same way as the radiometer crosses, *no* rotatory motion, even in bright sunlight. If, however, a screen of bright aluminum foil be placed as near as possible beneath it, the cross rotates even with a heavily clouded sky almost as quickly as the most delicate radiometers I have hitherto seen. The direction of rotation corresponds to an emission from the metallic surface."

If a *wire ring* is situated below the cross it becomes warmed in full sunlight, the molecules of gas rebounding from it transmit part of their *vis viva* to the mica plates and cause a rotation in the *normal* direction.

I may here refer to another explanation of the phenomena of motion in Zöllner's radiometer where the platinum ring is *traversed by an electric current.*

Nobody will doubt that the motion in a normal direction at a full atmospheric pressure is caused by currents of air produced by the heated wire. On the other hand it appears to me that Zöllner's view of the possibility of explaining the abnormal motion at smaller pressures than 10 mm. by an absorption of hydrogen by the platinum ring has less probability from the fact that this inversion was also observed by Zöllner himself with an aluminum ring, which certainly will only absorb hydrogen to a proportionately very slight extent. Moreover this reabsorption, and therefore also the motion, must some time come to an end, which is not the case. I am also of opinion that one would rather expect the *heated* wire to *exude* and not absorb gases.

I should be inclined to look for the cause of this inversion in the dielectric polarization and electrification of the mica plates. The wire traversed by a current will possess free electricity on its surface, which acts inductively on the mica laminæ and makes the sides turned towards it electrical.

I can, however, advance nothing with certainty as to how a pressure directed normally against the surface of the plate results from the electrical action of the platinum ring, which causes it to rotate in an abnormal direction, but I am none the less decidedly convinced of the electrical origin of this motion. The following experiment appears to me to point to this :—If one pole of the induction apparatus be connected with the platinum ring and the other be put to earth, and if the pressure in the radiometer is so great that by using the galvanic current an abnormal rotation would take place, the cross likewise rotates in an abnormal direction whether the positive or negative pole is put to earth.

If the action of the dielectric polarization is weaker than the action of the currents of air opposite to it, a normal rotation takes place according to Zöllner's statement from 760 to 10 mm.

If the galvanic current be broken whilst the radiometer is rotating in an abnormal direction, an inversion and rotation takes place in a *normal* direction. This rotation is caused by currents of air, and only lasts a short time because the wire rapidly cools down.

At high degrees of rarefaction a new cause of motion is superadded, viz. radiant heat, the action of which is also opposite to that of dielectric polarization. In consequence of greater rarefaction the wire becomes red hot, the intensity of the current smaller, and therefore also the mica plates less strongly electrical. The radiant heat of the platinum ring warms the mica plates on the sides facing it, and the reaction of the molecules rebounding with greater velocity from the mica plates, tends to turn the latter in a normal direction. As, moreover, heated gaseous molecules, that is those which are endowed with great velocities, issue from the platinum ring and transmit part of their *vis viva* to the vanes by collisions in the same sense, the *normal* rotation will be also thereby strengthened.

We can thus imagine a three-fold cause of the phenomena of motion in Zöllner's radiometer. Currents of air and thermal radiation tend to turn the plates in a *normal* and the action of the dielectric polarization in an *abnormal* direction. The currents of air decrease with the rarefaction, the action of the dielectric polarization predominates, and the first inversion takes place at 10 millim. On continued rarefaction the heating of the wire increases in consequence of the smaller thermal conductivity of the gas, and the intensity of the current decreases as well as the electrification of the mica plates, and since, moreover, the thermal radiation increases simultaneously, the action of the latter will predominate at a certain pressure, about 0·02 mm., and after a second inversion a *normal* rotation takes place.

If we could succeed in eliminating one action, *e.g.* that of heat, by replacing the platinum ring by a thick copper one, it is to be expected that the first inversion would take place at higher pressures than 10 mm., and that the second would perhaps not take place at all.

If this experiment, which I am thinking of next carrying out, is verified experimentally, it would be an indirect proof of the correctness of the explanation given by the electrification of the mica plates.

APPENDIX.

Whilst reading the proofs of my communication, "Contributions to the Explanation of Zöllner's Radiometer," I heard of a new paper of Prof. Zöllner, entitled *Das Scalen-Photometer* (Leipsic, 1879), which contains an answer to the objection I raised* to his theory of emission. Prof. Zöllner remarks in reference to this, "The presence of a small residue of gas, especially of oxygen, may very well favour a separation of the electrical particles by a sort of catalytic action, and thus cause a maximum effect of rotation at a certain degree of rarefaction."

With regard to this explanation I take the liberty of observing that I cannot feel convinced by it for this reason, that such catalytic actions as Prof. Zöllner assumes have not yet been *experimentally* demonstrated, and therefore possibly also do not exist. Hence a still more powerful support will be needed in order that the emission theory may hold its ground with the simple method of explanation by the kinetic theory of gases.

It may, too, be remarked that an experiment with the induction-current is given in the paper referred to, p. 59, which I have described on p. 321. Starting from this experiment Prof. Zöllner explains the *abnormal* rotation (by using an electrical current and a pressure of 10 to 0·02 mm.) as due to the existence of a *double current* of molecules of gas moving electrically, and indeed after the analogy of the double current of solid particles which are suspended in a liquid transmitting an electrical current, observed by Faraday, Armstrong, and Quincke. As to the mode of action of this double current Prof. Zöllner writes as follows :—

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* "Ueber das Radiometer." *Sitzungsberichte der Wiener Akademie*, vol. lxxx. 1879.

"If we therefore assume a similar relation between the large and small molecules in the rarefied spaces of the radiometer, which, however, are *always filled with mercury vapour*, and consider that at high densities of the vapours and gases the larger molecules will predominate, then the direction in which the mica cross *rotates* would really show the direction of the *ever present double current* of molecules of gas according to the degree of rarefaction."

Prof. Zöllner's view coincides with my own supposition as to the nature of the force which causes the abnormal rotation, but whilst I have openly confessed that I am still in doubt as to the *mode of action* of this force, Prof. Zöllner attempts an explanation which, even if supported by analogies, must first earn for itself recognition by further experiments.

Professor Gintl's Views on Radiant Matter.

In January 1880 the chemist Prof. Wilhelm Friedrich Gintl, of Prague, published a paper, "*Studien über Crookes strahlende Materie und die mechanische Theorie der Electricität*," in which he tries to answer the question from a purely critical point of view as to whether the assumption of the existence of a particular state of aggregation is really justified by the experiments of Mr. Crookes. This pamphlet, which was published by the author himself, was overlooked in the 1883 edition of the present collection of my papers, published in the Memoirs of the Royal Academy of Science of Vienna, because it had not come under my notice at that time. In taking the liberty, therefore, of calling the reader's attention to this interesting research, I need only say that Prof. Gintl, reasoning from a critical investigation of the phenomena described by Mr. Crookes in his lecture on "Radian Matter," arrives at the conclusion that Mr. Crookes's vie are not borne out by several phenomena observed by and that for the explanation of the phenomena in q

Fig. 1.

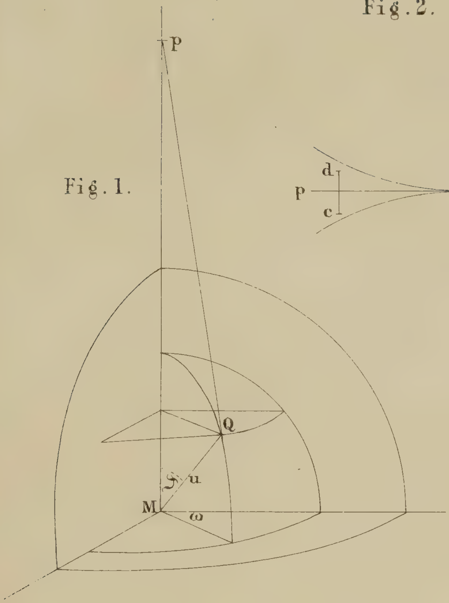


Fig. 2.

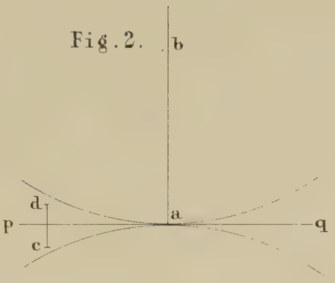


Fig. 3.

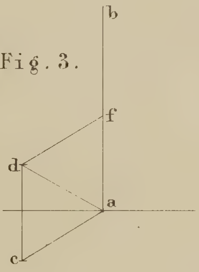


Fig. 4.

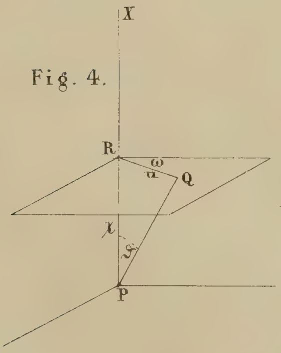
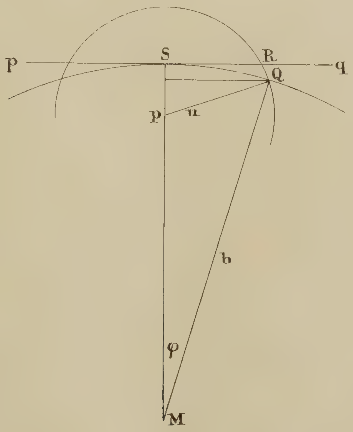


Fig. 5.

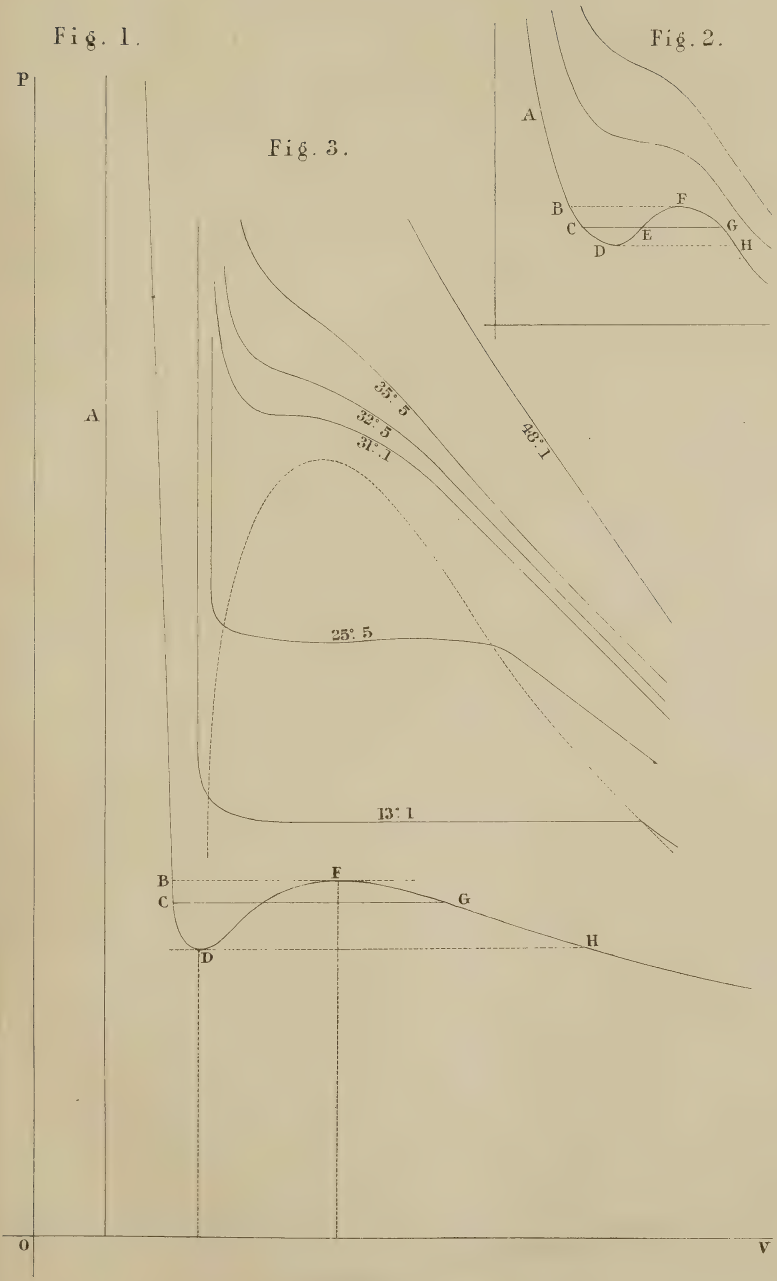


Mintern Bros. lith.

Fig. 1.

Fig. 2.

Fig. 3.



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PHYSICAL MEMOIRS.

THE CONTINUITY
OF THE
LIQUID AND GASEOUS STATES OF MATTER.

BY

PROFESSOR J. D. VAN DER WAALS.

CHAPTER I.

General Considerations.

[PLATES IV. & V.]

THE doctrine according to which the molecules of a body in molecular equilibrium remain at rest, and according to which the invariability of the distances of the molecules from one another depends on a repulsive force, has been generally abandoned. Such a doctrine is in fact in direct opposition to certain consequences drawn from the principle of the conservation of energy, and is in consequence untenable. Although the mechanical theory of heat, in order to be free from hypothesis, does not approach the question of the ultimate constitution of matter on which its laws depend, yet the assumption of a repulsive force between molecules, especially of gases, is neither in accordance with the above principle, with the conception of work, of potential and kinetic energy, nor with the doctrine of the equivalence of heat and work.

Let one particle be attracted by another with a force $=f(r)$, then, if the distance increases from r_0 to r_1, the work done against the forces of attraction is

$$\int_{r_0}^{r_1} f(r)\, dr.$$

This is expressed by the statement that potential energy to this amount is gained; and mechanics teaches that the same amount of kinetic energy disappears. Conversely, if a particle moves away under the influence of a repulsive force, a certain amount of potential energy is lost, and a corresponding amount of kinetic energy makes its appearance.

Finally, we learn from physics that where work is spent and does not completely and explicitly reappear as potential and kinetic energy, the excess produces an equivalent quantity of heat.

If we examine the experiments of Joule and Thomson by the light of the above considerations, we shall find that they are opposed to the doctrine of repulsive forces. For if the so-called permanent gases expand without overcoming external pressure, so far from their temperature being raised, it is in general lowered. But if we had to deal with a system kept in equilibrium by repulsive forces, there would be a diminution of potential energy corresponding to the increased space taken up by the gas after expansion, and the gas would rise in temperature. On the other hand, if the volume of a gas diminishes under an external pressure always equal to its own tension the potential energy must increase, and the temperature fall in consequence. The mechanical theory of heat could not under these circumstances establish the development of a quantity of heat equivalent to the external work done. Thus, the elasticity of a gas must be looked upon as a consequence of something other than molecular repulsion.

If, however, there is no repulsive force between the particles of a gas, we need not assume the existence of such a force to explain the properties of matter in its solid or liquid condition. Investigation also shows that in these states resistance .to diminution of volume is not to be ascribed to the action of a repulsive force in its proper sense. In liquid and solid bodies which expand by warming, heat is developed by compression, and indeed more heat than corresponds to the external work expended. Furthermore, if, in addition to the attraction of separate particles for one another, there is also a repulsion, and if an external pressure serves to overcome the excess of the repulsion over the attraction, then in this case also the work done would be wholly or partially recovered in the increase of the potential energy. Less heat would therefore be developed than that corresponding to the external work expended.

We have therefore to explain why it is that particles attracting one another and only separated by empty space do not fall together: and to do this we must look round for other causes. These we find in the motion of the molecules themselves, which must be of such a nature that it opposes a diminution of volume and causes the gas to act as if there were repulsive forces between its particles. With regard to the nature of this motion, more or less elaborate theories have been constructed for the different states of aggregation of matter. Especially for the so-called permanent gases, the researches of Clausius and Maxwell have resulted in the theory of molecular motion. Before we attempt to consider the nature of this motion in detail we will establish a theory of Clausius (1870), as to the relation between the kinetic energy of motion and the molecular attraction. Clausius gives this investigation in order to prove the Second Law of Thermodynamics by propositions borrowed from mechanics. We will follow his method, keeping in view the above-mentioned object.

CHAPTER II.

Derivation of the Fundamental Equation of the Isothermals.

LET us consider a number of particles occupying an invariable portion of space, and provisionally in motion. The result of our calculation will furnish us with a measure of this motion; so that if the measure vanishes the particles are at rest. As to the kind of motion, let us only suppose that it is "stationary," to adopt Clausius' expression; that is, that the distances of the particles from some arbitrary point are variable, but only within very narrow limits. In the cases in which the increase of the distances attains a sensible value we are to consider that the particles have changed places with one another. This condition is fulfilled by the particles of a body persisting in equilibrium. Let X, Y, Z be the components of the force acting on any particle at a given instant; and let x, y, z be the coordinates of the particle: it is required to find the values of ΣXx, ΣYy, and ΣZz.

For each particle we have

$$m\frac{d^2x}{dt^2}=X,$$

therefore

$$\Sigma Xx=\Sigma mx\frac{d^2x}{dt^2}.$$

Now

$$\frac{d\left(x\frac{dx}{dt}\right)}{dt}=x\frac{d^2x}{dt^2}+\left(\frac{dx}{dt}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

And since

$$x\frac{dx}{dt}=\frac{d\left(\frac{x^2}{2}\right)}{dt},$$

we may write (1)

$$\Sigma m\frac{d^2\left(\frac{x^2}{2}\right)}{dt^2}=\Sigma mx\frac{d^2x}{dt^2}+\Sigma m\left(\frac{dx}{dt}\right)^2$$

or

$$\Sigma Xx=\Sigma m\frac{d^2\left(\frac{x^2}{2}\right)}{dt^2}-\Sigma mV_x^2. \quad . \quad . \quad . \quad . \quad (2)$$

If the mass of each particle remains constant, we can bring m under the sign of differentiation, and according to the conception of stationary motion, can regard $\frac{mx^2}{2}$ as constant, so that

$$\Sigma \frac{d^2 m\left(\frac{x^2}{2}\right)}{dt^2} = 0,$$

while for the two other terms in (2), their mean value may be taken for a shorter or longer time.

In the case of periodic motion of common period, we may integrate (2) with respect to t, and if τ is the period of vibration, then for each particle (2) becomes

$$\frac{1}{\tau}\int_0^\tau \mathrm{X}\, x dt = \frac{m}{\tau}\left[\left(\frac{d\left(\frac{x^2}{2}\right)}{dt}\right)_\tau - \left(\frac{d\left(\frac{x^2}{2}\right)}{dt}\right)_0\right] - \frac{m}{\tau}\int_0^\tau \left(\frac{dx}{dt}\right)^2 dt\text{*}.$$

But since

$$\left(\frac{d\left(\frac{x^2}{2}\right)}{dt}\right)_\tau = \left(\frac{d\left(\frac{x^2}{2}\right)}{dt}\right)_0$$

the terms between the square brackets vanish, while the remaining terms represent the mean values of $\mathrm{X}x$ and $\mathrm{V}_x{}^2$.

If the motion is not periodic the difference

$$\left(\frac{d\left(\frac{x^2}{2}\right)}{dt}\right)_\tau - \left(\frac{d\left(\frac{x^2}{2}\right)}{dt}\right)_0$$

does not necessarily vanish. But according to the conception of stationary motion $\frac{mx^2}{2}$ is capable of a small variation only. In addition to this we may increase the quantity τ which is the divisor of the difference. The difference itself cannot increase continuously, from which we gather that τ may be so chosen that in this case also the equation holds, and expresses that the mean values of $-\Sigma \mathrm{X}x$ are equal to the mean values of $\Sigma m \mathrm{V}_x{}^2$.

If the particles are not all of the same mass, we must regard the body either as a mixture or as a chemical combination; and in this case also the corresponding equation holds good for each set of particles, under the same suppositions.

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* Routh, Rigid Dynamics, p. 282; Clausius, Phil. Mag. Aug. 1870.

So that, finally, in every case we have

$$(\text{mean}) - \Sigma Xx = (\text{mean})\ \Sigma m V_x^2 . \quad . \quad . \quad . \quad (3)$$

$$(\text{mean}) - \Sigma Yy = (\text{mean})\ \Sigma m V_y^2 . \quad . \quad . \quad . \quad (4)$$

$$(\text{mean}) - \Sigma Zz = (\text{mean})\ \Sigma m V_z^2 . \quad . \quad . \quad . \quad (5)$$

Writing

$$V_x^2 + V_y^2 + V_z^2 = V^2,$$

adding (3), (4), and (5), and dividing by 2, we get

$$\Sigma \frac{m}{2} V^2 = -\tfrac{1}{2}\Sigma (Xx + Yy + Zz) . \quad . \quad . \quad . \quad (6)$$

If there are only attractive forces between the particles of the body, or if in addition an inwardly directed pressure is necessary to keep them in equilibrium, then the right-hand side of our equation (6) can have a positive value only, and cannot vanish. By throwing the right-hand side of the equation into other forms this property will become clear.

Thus the particles are in motion, and we can form an expression for the kinetic energy of this motion. In the case of very highly rarefied gases in which we may provisionally neglect the mutual attraction of the particles, experience teaches us that external forces are necessary to maintain a condition of equilibrium. In this case X, Y, Z represent the components of the forces which act perpendicularly to the surface and take the place of the deficient attractive forces.

Before we draw any further conclusion from equation (6), we must endeavour to find some other form into which $\Sigma (Xx + Yy + Zz)$ can be put.

Let the force acting on a particle be R, and let the angles which its direction makes with the axes be α, β, γ. If we take the distance from the origin of the particle on which the force acts as r, and the angles made by r with the axes as $\alpha_1, \beta_1, \gamma_1$, then $\Sigma (Xx + Yy + Zz)$ becomes

$$\Sigma Rr (\cos\alpha \cos\alpha_1 + \cos\beta \cos\beta_1 + \cos\gamma \cos\gamma_1)$$

or

$$-\Sigma Rr \cos (Rr) = \Sigma m V^2 . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The force which the particle a exerts on the particle b is equal and opposite to that exerted by b on a. Let this force be attractive and equal to f. Then the sum of the two expressions arising from the force between a and b can be reduced to a very simple form in the following way. The expression arising from the attraction of b on a is $f\,r\cos(f, r)$ and for a on b is $-fr_1\cos(f, r_1)$. But $r\cos(f, r)$ is the projection of r on the line ab, and $r_1\cos(f, r_1)$ is the projection of r_1 on the same line. The difference of these projections is the line itself. So the sum of the two expressions, when ρ is the distance between the points, becomes equal to $f\rho$. In consequence of this, equation (6) becomes

$$\Sigma\frac{m}{2}V^2=\tfrac{1}{2}\Sigma f\rho-\tfrac{1}{2}\Sigma Rr\cos(R\,r). \quad . \quad . \quad . \quad (8)$$

In the last equation $\Sigma f\rho$ refers to all the molecular forces, the force between any two molecules being only reckoned once. Moreover the second term of the right-hand side refers entirely to external forces.

Equation (8) may also be obtained directly from (6) without the help of (7).

The expression Xx becomes for the point a

$$=\frac{fx(x_1-x)}{\rho},$$

and for the point b

$$=-\frac{fx_1(x_1-x)}{\rho}.$$

Their sum is equal to

$$-\frac{f(x_1-x)^2}{\rho},$$

Similarly for Yy we get

$$-\frac{f(y_1-y)^3}{\rho},$$

and for Zz

$$-\frac{f(z_1-z)^2}{\rho}$$

Thus for the force between a and b we get

$$Xx+Xy+Zz=-f\rho.$$

In order to derive the expression arising from the external forces, let us assume that the pressure is equally distributed over the whole surface and acts perpendicularly to it; and that gravity is neglected. For this purpose we take advantage of a theorem of Green which has been of great service in the theory of Electrostatics. This theorem is generally written

$$\int \nabla^2 V dk = \int \frac{dV}{dn} dS. \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

V is a function of x, y, z; dk an element of volume; and the integration is to be extended to all the points within the prescribed space. The expression $\frac{dV}{dn}$ is the so-called differential coefficient of V with respect to the normal to the surface of which dS is an element. The integration of the second term must be extended to all points of the surface.

Let N be the value of the normal pressure per unit area of surface; we have to evaluate

$$\int Nr \cos (Nr)\, dS$$

or

$$\tfrac{1}{2} N \int \frac{d(r^2)}{dr} dS \cos (Nr).$$

But

$$\frac{d(r^2)}{dn} = \frac{\partial(r^2)}{\partial x}\frac{dx}{dn} + \frac{\partial(r^2)}{\partial y}\frac{dy}{dn} + \frac{\partial(r^2)}{\partial z}\frac{dz}{dn}$$

$$= 2 \left\{ x \cos (NX) + y \cos (NY) + z \cos (NZ) \right\}$$

$$= 2r \cos (Nr) = \frac{d(r^2)}{dr} \cos (Nr).$$

Substituting this value in the integral it takes the form

$$\tfrac{1}{2} N \int \frac{d(r^2)}{dn} dS,$$

and from (A) we have this equal to

$$\tfrac{1}{2} N \int \nabla^2 (r^2) dk = 3Nv,$$

where v is the whole volume*.

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* [This is the subject of a note in the German edition, giving a reference

Further, for a uniform normal pressure, equation (8) becomes

$$\Sigma\,\tfrac{1}{2}mV^2=\tfrac{1}{2}\Sigma f\rho+\tfrac{3}{2}Nv. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The reduction of

$$\int Nr\cos(Nr)\,dS$$

to the form 3Nv is accomplished more easily, as follows. The element $r\cos(Nr)\,dS$ is three times the volume of a pyramid, having the origin at the vertex, dS for base, and whose height is $r\cos(Nr)$. Summing these pyramids over the whole surface and reckoning as negative those for which $\cos(Nr)$ has a negative value, we obtain three times the volume of the body.

Let us now consider a gas as consisting of points of mass exerting no attraction on one another, then the expression $\frac{1}{2}\Sigma f\rho$ disappears from equation (9), and we obtain Clausius' equation

$$\Sigma\,\tfrac{1}{2}mV^2=\tfrac{3}{2}Nv. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Let $V_1{}^2$ be the mean value of the square of the velocity; then (10) becomes $\frac{1}{2}MV_1{}^2=\frac{3}{2}Nv$. If δ is the weight per unit volume and g the acceleration due to gravity, then $M=\dfrac{v\delta}{g}$; and (10) may be written

$$V_1{}^2=3N\frac{g}{\delta}=3N\frac{g}{\delta_0}(1+\alpha t). \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The pressure (N) is reckoned in kilograms weight per square metre, and the density in kilograms per cubic metre; g and V_1, are expressed in terms of metres and seconds.

An hypothesis exactly opposite to that made in the treatment of gases may be similarly used as a basis for the treatment of liquids. In this case we may neglect the external pressure; while, on the other hand, we must take into account the molecular forces. These forces balance the continual tendency to separation which results from the molecular motion.

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to Beer's *Electrostatik*, p. 15. The proof of this proposition is, however, so well known, that it is only necessary to indicate that for V we must substitute $x^2+y^2+z^2=r^2$ in (A).]

We may consider it as proved that molecular forces act at very small distances only, and that their intensity diminishes so rapidly with increase of distance as to become insensible when the distance itself becomes measurable. Researches on the distance at which molecular forces become insensible have not so far yielded concordant results; they agree, however, in showing that this distance is very small. In fact the generally received opinion that the molecular attraction is insensible in gases amounts to an admission of the narrow range of molecular forces.

We may also consider that experiment has fully proved that when a liquid is of the same temperature throughout it is as a rule of the same density at every point. But the density of a very thin layer at the surface may differ from the density within the liquid; though as far as experiments have yet been made the thickness of the layer has proved itself too small for measurement.

Moreover, if we treat the elementary parts of a liquid as "particles," a treatment which we have already applied to gases, we can bring equation (6) referring to the case of liquids into a form exactly corresponding to equation (10), which we deduced as referring to gases.

Since we assume that there is no external pressure, X, Y, Z will refer to those forces alone which are due to the mutual action of the particles. It follows from our first remark as to the narrowness of range of these molecular forces, that we need only take into account (in considering the force on any given particle) those other particles which are within a sphere of very small radius having the particle as centre, and termed the "sphere of action," the forces themselves becoming insensible at distances greater than the radius of the sphere.

From our second remark as to the constancy of density throughout a liquid it follows that all those points will be in equilibrium about which we can describe a sphere of action without encroaching on the boundary. By this of course is meant that the particles will be in equilibrium as far as attraction alone is concerned; not necessarily so when the molecular motion is also taken into account—though this will actually be the case for the mass taken as a whole. In other words, the forces X, Y, Z are zero for all points within the mass. Consequently the expression $\Sigma(Xx+Yy+Zz)$ vanishes. We thus find a great similarity between the relations we have discovered for the particles of a liquid and for the particles of a gas. On the particles of a gas no forces act; on the particles within a liquid the forces neutralize each other. In both cases the motion will go on undisturbed so long as no collisions occur.

The particles for which the forces may be put equal to zero constitute *à priori* by far the greater part of the mass, leaving only a comparatively small number on which uncompensated forces act. These last lie on the boundary and form a layer whose thickness is the radius of the sphere of action; and the forces on these particles are directed inwards. If about one such particle we describe the sphere of action, part of this sphere will be external to the liquid, and this part will represent the space which would be occupied by the particles which would if present annul the forces. So the remaining force acting inwards is equal in magnitude to the attraction which the particle in question would have experienced from the action of the particles which are absent. Later on we shall develop formulæ for this force; and also show how its amount per unit area of surface changes with the form of the surface; for the present, however, it will suffice to determine its direction. For this purpose we will consider that the surface is spherical, both because this will allow us to consider the force as constant at every point and because a sphere is the only form which can be assumed by a liquid not acted on by external forces. From the principle of the freedom of motion of the particles of a liquid the force may be taken as perpendicular to the surface at every point, independently of its form. All liquids do not, however, exhibit the phenomenon of mobility to the same degree, so we shall exclude those which in this respect approach the solid condition.

Thus we reach the conclusion that at the surface of a liquid there are normal forces acting inwards. It is true that the points of application of these forces are not exactly in the surface; but on account of the small thickness of the layer considered, their transference to the surface will hardly affect the result. We are thus led to the same conclusion for the case of liquids which we have already reached for that of gases, namely, that there are no forces *within* the mass considered, while the forces at the boundary are normal to it. In fact if N is the value of this boundary force per square metre of surface we obtain

$$\Sigma\tfrac{1}{2}mV^2=\tfrac{3}{2}Nv \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

just as we did before.

If we had not transferred all our forces to the surface we should have had to consider their action distributed over a number of layers through a thickness equal to the radius of the sphere of action. Let N_1, N_2, etc. be the forces, and v_1, v_2, etc. the volumes within different layers. Then we get

$$\Sigma\tfrac{1}{2}mV^2=\tfrac{3}{2}\Sigma_1^n N_n v_n.$$

Calling N the sum of N_1, N_2, etc., v the whole volume of the liquid, and v_1 the volume within the surface layer, we have

$$\tfrac{3}{2}Nv>\Sigma\tfrac{1}{2}mV^2>\tfrac{3}{2}Nv_1.$$

In cases where v and v_1 do not sensibly differ, we may rest satisfied with equation (12).

Forming an intermediate state between liquids, in which we assume no external pressure, and gases, in which we omit molecular forces, we have the state in which both terms occur. As a matter of fact, we shall see further on, that this is the only state which occurs in nature. The molecular attraction which we have assumed is shown by experience to be insufficient to resist the effect of molecular motion. Indeed the condition of very dense gases or vapours is much more nearly allied to the condition of the so-called perfect gases than to that of liquids ; since they require containing vessels to keep them of a prescribed volume.

In this intermediate or real condition of aggregation, $-\Sigma(Xx+Yy+Zz)$ refers both to external and internal forces. Evaluating this expresssion first for external forces we find immediately that its value is $\tfrac{3}{2}Nv$, just as in the case of gases. A similar form of expression must be obtainable from the above sum for the molecular forces. In vapours each portion of the interior is in equilibrium ; and regarding the "parts" as "particles," the sum of the expressions for the forces acting on them will vanish, leaving those forces only which act on the parts of the external layer; and which without further proof may be taken as acting on the surface, and regarded for purposes of calculation as an increase of the external pressure. In the case we are treating (that of vapours) this external additional pressure will be much smaller than in the case of liquids, because as a rule the density of vapours is much less than that of liquids. In other words, the quantity of matter within a given portion of the sphere of action is much less in one case than in the other; and since it may well be that in molecular attraction the force is proportional to the masses in action, there will in the case of vapours be a small molecular force only. Supposing that N_1 represents the value of this molecular pressure per square metre, equation (6) becomes for vapours

$$\Sigma\tfrac{1}{2}mV^2=\tfrac{3}{2}(N+N_1)v. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

In this equation is contained the proposition, that for bodies in the state of vapour the product of the external pressure into the volume is less than it is, on the supposition that we are dealing with a perfect gas. In order to get a constant product we must multiply v by $N+N_1$ and not by N. The difference N_1v between the value of the true product got by multiplying the volume by the true pressure and that obtained from experiment, affords information as to the value of the molecular forces. If this difference were to remain constant, it would follow that at constant temperature the molecular pressure is inversely proportional to the volume. We have, however, no reason *à priori* to think that such is really the case; and, as we shall see later on, it is rather to be expected that the pressure will turn out to be proportional to the square of the density. In this case N_1v will increase when the volume diminishes; a result quite agreeing with the fact that in imperfect gases the product of the pressure by the volume diminishes with increase of pressure.

If a liquid is subject to external pressure which, as we know, must be uniform and normal to the boundary (gravity being supposed not to act), then (6) immediately takes the form

$$\Sigma\tfrac{1}{2}mV^2=\tfrac{3}{2}(N+N_1)v,$$

as in the case of vapours; though it must not be lost sight of that the ratio of N to N_1 is very different.

In liquids, N_1 is generally far greater than N; and hence the small compressibility of liquids for pressures of the order of an atmosphere ought not to surprise us. In fact the compressibility is in reality so small as formerly to have led to the belief that liquids were incompressible.

Equation (13) gives a relation between v and N. Supposing the temperature and therefore V to remain constant, then taking v as abscissa and N as ordinate we get the curves generally called Isothermals. This relation holds unchanged if we regard the molecules as particles; but since this is not accurately the case, (13) will need a correction before it is applicable to matter as it really exists. This correction will be given later; N_1 must appear in it as a function of v. Equation (13) can therefore be considered as the fundamental equation of the Isothermals.

CHAPTER III.

Analytical Expression for the Molecular Pressure.

WE proceed to develop an analytical expression for the molecular pressure in a group of particles mutually reacting with forces which vanish at a sensible distance.

To obtain one of the expressions for this force we shall follow Laplace (*Méc. Cél.* t. iv.).

First, let us determine the attraction of a sphere on an infinitely thin cylinder normal to the sphere and outside it.

Let M (Plate IV. fig. 1) be the centre of the given sphere, P a point of the liquid column, and $MP=r$. About M describe an infinitely thin spherical shell of radii u and $u+du$. The volume of an element of this shell is $u^2du \sin\theta \, d\theta \, d\omega$, where θ is the angle between MP and MQ, and ω is the angle between the plane PMQ and a fixed plane. If f is the distance PQ, then

$$f^2=r^2+u^2-2ur\cos\theta.$$

Denoting the force exerted by unit mass at Q on the particle at P by $\phi(f)$, and the density of the sphere by D, then

$$Du^2du \sin\theta \, d\theta \, d\omega \, \phi(f) \cos(fr)$$

is the component along PM of the force exerted by the element at Q on P.

If $\phi(f)$ is the force, then $\int\phi(f)df$ is the work done, and this integral between the limits ∞ and f can be written $c-\pi(f)$. Here c denotes the potential energy of P when at an infinite distance from unit of mass at Q, and $\pi(f)$ is the potential energy lost in approach to distance f; so that $c-\pi(f)$ is the quantity still available at P due to unit mass at Q.

If f has a sensible value, then $c-\pi(f)$ is as great as it is at an infinite distance, and $\pi(f)$ is zero. Thus

$$\mathrm{D}u^2du\sin\theta\, d\theta\, d\omega\{c-\pi(f)\}$$

denotes the potential energy of P due to the presence of the element at Q. By differentiating this with respect to r we get the force along r, as is verified from the equality of $\cos(fr)$ and $\frac{df}{dr}$.

Integrating first with respect to ω, we get the potential energy of P due to a ring through Q whose plane is perpendicular to MP. The limits for ω are $\omega=0$ and $\omega=2\pi$. The integral becomes

$$2\pi\mathrm{D}u^2du\sin\theta\, d\theta\{c-\pi(f)\}.$$

This is to be integrated with respect to θ. The first term gives between $\theta=0$ and $\theta=\pi$ the value $4c\pi\mathrm{D}u^2du$. The second term takes the form

$$-2\pi\mathrm{D}\frac{u^2du}{ur}\int fdf\pi(f),$$

as appears by using

$$\sin\theta\, d\theta=\frac{fdf}{ur},$$

which is got by differentiating

$$f^2=r^2+u^2-2ru\cos\theta.$$

The limits of f are

$$\text{for } \theta=0, f=r-u, \quad \text{and for } \theta=\pi, f=r+u.$$

Let $$-\int fdf\pi(f)=\psi(f),$$

then $\psi(f)$ must be such as to vanish for finite values of f;

and the available potential energy of P due to the spherical shell is

$$4\pi c \mathrm{D} u^2 du + 2\pi \mathrm{D} \frac{u}{r} du \{\psi(r+u) - \psi(r-u)\}.$$

In order to get the attraction on P along r we should have to differentiate with respect to r. In order to find the attraction exerted on the whole liquid column we should integrate with respect to r, and of course get the original function. Evidently the liquid column must have the same density throughout, as Laplace seems to suppose everywhere in his development. If the liquid column begins at a distance b measured from M, the attraction must vanish for $r=b$. Hence

$$2\pi \mathrm{D} \frac{u}{r} du \{\psi(r+u) - \psi(r-u)\} - 2\pi \mathrm{D} \frac{u}{b} du \{\psi(b+u) - \psi(b-u)\}$$

is the attraction exerted by the liquid shell on the column of uniform density and height $r-b$. If the column is of finite height we may put $\psi(r-b)=0$, as also

$$\psi(r+u), \quad \psi(b+u), \quad \text{and } \psi(r-u).$$

There remains for the attraction

$$2\pi \mathrm{D} \frac{u}{b} du \, \psi(b-u),$$

and this expression has an appreciable magnitude only when $b-u$ is extremely small.

Finally, to find the attraction of the whole sphere, we must integrate with respect to u. Supposing the liquid column to be in contact with the sphere the limits are $u=0$ and $u=b$, and the whole attraction becomes

$$\frac{2\pi}{b} \int_0^b \mathrm{D} u \, du \, \psi(b-u).$$

If D is constant it may be taken outside the sign of integration and the attraction becomes

$$\frac{2\pi \mathrm{D}}{b} \int_0^b u \, du \, \psi(b-u).$$

For a sphere of variable density this should at least be constant throughout concentric spherical shells, and now for the first time we have to deal with a possible variation of density. By a former remark we are justified in putting the variable density of a liquid in equilibrium equal to

$$D\{1-f(b-u)\},$$

where $f(b-u)$ is zero for finite values of $b-u$. In the last integral, substituting z for $b-u$, we get

$$2\pi D\int_0^b \frac{b-z}{b}dz\,\psi(z),$$

or, supposing the liquid column of density D instead of 1 as before,

$$2\pi D^2\int_0^b \frac{b-z}{b}dz\,\psi(z),$$

or

$$2\pi D^2\int_0^b \psi(z)dz-\frac{2\pi D^2}{b}\int_0^b z\,dz\,\psi(z).$$

If we increase the upper limit indefinitely (see Laplace, *Méc. Cél.* Suppl. to Book X. Sec. 1), this becomes

$$2\pi D^2\int_0^\infty \phi(z)dz-\frac{2\pi D^2}{b}\int_0^\infty z\,dz\,\psi(z).$$

In this form the attraction which a thin column of liquid experiences from a sphere consists of two terms, one of which is independent of the size of the attracting sphere, and the other is inversely proportional to the radius of the sphere; it may be written $K-\frac{H}{b}$.

It is easy to see the meaning of K. Taking $b=\infty$, K is the attraction exerted by the liquid on an infinitely thin column in contact with the plane boundary of the liquid. Then $\frac{H}{b}$ must be the attraction exerted by a liquid mass contained between a tangent plane and a sphere of radius b.

Evidently H is far smaller than K; since each element of K must be multiplied by z to give a corresponding element of H. It is, however, only for very small values of z that $\psi(z)$ has a finite value; and in the present calculation it is just when z reaches its highest values that $\psi(z)$ is smallest. It is to be especially remarked that $K-\frac{H}{b}$ also denotes the attraction exerted on the liquid column by a part only of the sphere, viz., that part adjacent to the column which does not exceed in extent the radius of the sphere of action.

We proceed to find the attraction exerted on an infinitely thin liquid column within the mass and with one end resting on the spherical surface.

For this purpose we determine the attraction on *ab* (Plate IV. fig. 2) of a mass of which one part lies below *pq*, and the other between *pq* and the image in *pq* of the original spherical surface. Let *c* and *d* be images of each other; then *cd* is parallel to *ab*, and *c* is as much below *a* as *d* is above, and *ab* will be equally attracted downwards by each. This appears from Plate IV. fig. 3, where, taking $df = ac$ or *ad*, we see that *af* is not attracted downwards by *d*. Thus, the part of *ab* attracted by *c* is situated with respect to *c* in the same way as the part attracted by *d* is situated with respect to *d*.

Hence the attraction of a liquid mass, with a spherical hollow, on a column outside the mass and normal to the spherical surface, exceeds K by as much as the attraction of the sphere alone is less than K. And since to maintain the column in equilibrium it is necessary and sufficient to fill up the hollow, the attraction of a sphere on a column within it, as described, becomes $\mathrm{K} + \frac{\mathrm{H}}{b}$.

Finally, in order to investigate the force which acts inwardly on an infinitely thin column situated inside a liquid and standing perpendicular to its surface, this last being of any arbitrary form, we may proceed as follows :—

At the point where the liquid column rests on the surface, draw a tangent plane to the surface; then, in the case when the mass occupies the whole space on one side of the tangent plane, the force exerted on the column is K. If this is not the case, we have to find the attraction exerted by the part of the liquid mass between the tangent plane and the surface, or if the surface is convex by the part which is wanting there. For this purpose, consider two planes through the normal to the surface inclined to each other at the small angle $d\theta$. This angle cuts from the attracting mass a part which may be considered equal to the part taken away from a liquid mass bounded on one side by the tangent plane and on the other by a spherical surface, the radius of this surface being the radius of curvature of the section of the surface made by one of the planes which form the angle.

Measuring θ from one of the principal sections of the surface, and denoting by R and R_1 the principal radii of curvature, then the radius of curvature of the section which makes the angle θ is given by

$$\frac{1}{\rho}=\frac{\cos^2\theta}{R}+\frac{\sin^2\theta}{R_1}.$$

If $\frac{H}{\rho}$ is the attraction exerted on the liquid column by a mass filling the whole space between the tangent plane and the sphere of radius ρ, then $\frac{H}{\rho}\frac{d\theta}{2\pi}$ will denote the attraction due to the part within the infinitely small angle, and thus the whole attraction becomes

$$\int_0^{2\pi}\frac{H}{\rho}\frac{d\theta}{2\pi}=\frac{H}{2\pi}\int_0^{2\pi}\left(\frac{\cos^2\theta}{R}+\frac{\sin^2\theta}{R_1}\right)d\theta=\frac{H}{2}\left\{\frac{1}{R}+\frac{1}{R_1}\right\},$$

and finally the attraction takes the form

$$K+\frac{H}{2}\left\{\frac{1}{R}+\frac{1}{R_1}\right\},$$

where the radius of curvature is taken negative when the liquid section is concave towards the observer.

In addition to this we will give another method of calculating the molecular pressure on the surface arising from a number of mutually attracting particles. For this purpose we will determine the attraction exerted on the point P (Plate IV. fig. 4) by a liquid mass placed immediately over it, and supposed to be divided into parallel layers. Drop a perpendicular from P on to one of these layers; and from the point where it meets the layer let there be a line of length u drawn in the plane of the layer to a liquid particle Q. If dx is the thickness of the layer, the element surrounding the point Q will have a volume $u\,du\,d\omega\,dx$. If we take θ as the angle contained between the line PQ and the normal, and put PQ$=f$, then

$$u=x\tan\theta,\quad\text{and}\quad du=x\frac{d\theta}{\cos^2\theta};$$

and the element of volume becomes

$$dx\, x \tan\theta\, x \frac{d\theta}{\cos^2\theta} d\omega.$$

As before, assuming the law of force to be $\phi(f)$, and the density constant, we get as the attraction of Q on P perpendicular to the layer

$$d\omega\, dx\, x \tan\theta\, x \frac{d\theta}{\cos^2\theta} \phi\left(\frac{x}{\cos\theta}\right) \cos\theta.$$

Reducing the last expression, we have

$$dx\, x^2 d\left\{\frac{1}{\cos\theta}\right\} \phi\left(\frac{x}{\cos\theta}\right) d\omega.$$

Integrating with respect to ω between $\omega=0$ and $\omega=2\pi$, we get for the attraction of the ring passing through Q,

$$2\pi x^2\, dx\, d\left\{\frac{1}{\cos\theta}\right\} \phi\left(\frac{x}{\cos\theta}\right).$$

In order to obtain the attraction of the whole layer, we must integrate with respect to θ, keeping x constant, between the limits

$$\theta=0 \quad \text{and} \quad \theta=\frac{\pi}{2},$$

or, what comes to the same thing,

$$x=\frac{x}{\cos\theta} \quad \text{and} \quad \infty=\frac{x}{\cos\theta}.$$

This gives us

$$2\pi\, x\, dx \int_x^\infty \phi\left(\frac{x}{\cos\theta}\right) d\left(\frac{x}{\cos\theta}\right).$$

Putting, in the same way as before,

$$\int \phi(x)\, dx = \mathrm{C} - \pi(x),$$

the attraction of the whole layer becomes $2\pi\, x\, dx\, \pi(x)$. $\pi(x)$ vanishes for finite values of x.

In order to find the attraction of a liquid cylinder on P, we must evaluate

$$2\pi \int_x^\infty x\, \pi(x)\, dx.$$

Again putting $\int x\, \pi(x)\, dx$ equal to $\mathrm{C}_1 - \psi(x)$, we get

$2\pi\psi(x)$ as the value of the integral; $\psi(x)$ being again a function which vanishes for finite values of x. Hence $\psi(x)$ appears to have the same meaning by this method as we found it had by the other. This function is the law of force for an element of liquid at distance x from a cylinder of liquid bounded by a plane surface. But the elements of the cylinder which are further away from the attracted point than the radius of the sphere of action exert no attraction. So that $\psi(x)$ also denotes the law of force for an element of the liquid forming a spherical segment of the sphere of action at a distance x from the particle.

We may make use of this remark to determine the force which is exerted inwards on an infinitely thin liquid column by a liquid having a plane boundary.

Take an element of the column of thickness dx, where x is the distance of the element below the surface of the liquid. Taking this point as the centre of the sphere of action, we find that when the radius of this sphere is greater than x it partly lies outside the liquid. It clearly follows that the force with which the element is attracted inwards amounts to $2\pi\psi(x)dx$. For the whole column, as before, this becomes

$$2\pi\int_0^\infty \psi(x)\,dx = \mathrm{K}.$$

Also we can find a signification for each element of the integral $2\pi\int\frac{x}{b}\,\psi(x)\,dx$, which, in the case of a spherical surface, must be added to $2\pi\int\psi(x)dx$ to give the molecular pressure.

Describing the sphere of action round P (Plate IV. fig. 5), a particle of the surface-layer, it is easy to see that P is attracted inwards by a force equal to that which would be exerted by a liquid occupying the vacant part of the sphere. We know the force exerted by the spherical segment to be $2\pi\psi(a)$, where a is the distance of P from the tangent plane. We will now show that $2\pi\frac{a}{b}\psi(a)$ is the force which would be exerted by the remaining vacant part of the sphere of action, were it filled with liquid.

Drawing a spherical shell, of radii u and $u+du$, this occupies a space between the tangent plane and the spherical surface equal to $2\pi u\,du(b-b\cos\phi)$. Here b is the radius of the sphere, and ϕ the angle between the radius through P and a line drawn through the centre to a point of section of the shell with the liquid surface. We easily find the value of $b-b\cos\phi$ to be $\frac{u^2-a^2}{2(b-a)}$ from the triangle which has its sides respectively equal to u, $b-a$, and b. Thus

$$u^2=b^2+(b-a)^2-2b(b-a)\cos\phi,$$

or

$$u^2-a^2=(b^2-a^2)+(b-a)^2-2b(b-a)\cos\phi,$$

and

$$u^2-a^2=(b-a)\{2b-2b\cos\phi\}.$$

Putting, as above, $\pi(u)$ for the potential energy lost by a unit mass of liquid during the approach of a particle from infinity to a distance u, we get for the loss experienced by the part of the spherical shell between the surface and the tangent plane, $2\pi u\,du\frac{u^2-a^2}{2(b-a)}\pi(u)$.

Since a is very small compared with b, we shall not greatly diminish the value of this by simplifying it to

$$2\pi u\,du\frac{u^2-a^2}{2b}\pi(u).$$

By differentiating this with respect to a and changing sign, we get the force exerted by the prescribed portion of the spherical shell on a. This amounts to

$$2\pi u\frac{a}{b}\pi(u)\,du.$$

In order to find the force exerted by the whole mass between the tangent plane and the surface, we have to integrate with respect to u, from $u=a$ to $u=\infty$. Remembering that $\psi(\infty)=0$, we get

$$2\pi\frac{a}{b}\psi(a),$$

putting, as above,

$$\int u\,\pi(u)\,du=C_1-\psi(u).$$

For the infinitely thin column of which P is a portion, the attraction is

$$2\pi\int_0^\infty \frac{x}{b}\,\psi(x)\,dx.$$

The value of K for liquids is yet unknown; we shall, however, in the sequel find that its value for water amounts to several thousand atmospheres. The value of H, on the contrary, has on many occasions formed the subject of experimental investigations. The difficulty which besets the determination of K lies in the fact that the form of a quantity of liquid in no way depends on its value. On the other hand, it is the quantity which, in conjunction with the molecular motion, fixes the volume of the liquid and thus resembles the external pressure, which, in connexion with the molecular motion, determines the volume of a gas. The form of a liquid, setting aside external forces, depends on H, as is clear from the expression for the molecular pressure, in which it occurs multiplied by $\frac{1}{2}\left(\frac{1}{R}+\frac{1}{R_1}\right)$. The same quantity also has some effect on the volume; although its influence in this respect is small, since it is small itself, as appears from what precedes. As the method of determining H belongs to the theory of capillarity, we will take it as known, and limit ourselves to stating the value of H for water. This value is about 16·4 mg. weight per linear millimetre, and when multiplied by $\frac{1}{2}\left(\frac{1}{R}+\frac{1}{R_1}\right)$ is added to the normal pressure K exerted on the liquid at the boundary surface, just as if this latter were an elastic sheet acting on a number of perfectly mobile particles contained within it. If we regard the boundary surface as acting like an elastic film, we must suppose that a strip of this film one millimetre wide is tending to contract with a force equal to the weight of 8·2 mg.

This will become clear from a consideration of the case of a spherical mass of liquid. Suppose such a mass to be divided by any plane passing through the centre, and let α represent the tension per unit length perpendicular to the periphery of a ribbon one millimetre wide running round the sphere. Then the upper and lower hemispheres will be drawn together with a force equal to $2\pi r\alpha$.

If σ is the pressure thereby set up per square millimetre in the interior of the sphere, then $\pi r^2\sigma/mg$ will represent the pressure on the plane surface of the hemisphere. Thus

$$2\pi r\alpha = \pi r^2\sigma,$$

and

$$\frac{2\alpha}{r} = \sigma = \frac{\text{H}}{r}, \quad \text{or} \quad \text{H} = 2\alpha.$$

For a surface of any form we should be led in like manner to the same conclusion.

We must, however, be careful not to push the analogy with an elastic film too far. In the case of the liquid surface the tension is constant if the temperature does not change, and it is quite independent of the extent of the surface. If the surface increases, molecules originally in the interior make their appearance at the surface; while if a diminution of surface occurs, an exactly opposite phenomenon takes place. In relation to the attraction due to gravity, H is a quantity of very considerable magnitude; the amount of matter contained in a square millimetre of active film is so small that a force of 16·4 mg. weight must be treated as large compared with the attraction of gravity on it. Thus, in very thin liquid films, we may neglect the action of gravity altogether.

On the other hand, in great quantities of liquid the action of gravity is vastly more important than that part of the action of the molecular forces depending on the quantity H. For instance, a large drop of quicksilver on a table is far from being spherical, as it would be were gravity negligible.

We have now to develop the expression

$$\Sigma\, \tfrac{1}{2}m\text{V}^2 = \Sigma\, \tfrac{1}{2}(\text{X}x + \text{Y}y + \text{Z}z)$$

for a mass of liquid subject to the action of gravity, and on the supposition that the body forming the support exerts no other influence than to support it.

In this case the molecular pressure acts on the surface, and gravity throughout the mass of liquid. The normal pressure is no longer constant, but increases with the depth. Let R and R_1 be the principal radii of curvature at the highest point of the liquid at a distance h from the horizontal plane. The pressure here is

$$\text{K} + \frac{\text{H}}{2}\left(\frac{1}{\text{R}} + \frac{1}{\text{R}_1}\right);$$

and in a layer at a height z, if D is the weight per unit volume of the liquid,

$$\mathrm{K}+\frac{\mathrm{H}}{2}\left(\frac{1}{\mathrm{R}}+\frac{1}{\mathrm{R}_1}\right)+\mathrm{D}(h-z).$$

If ρ and ρ_1 are the principal radii of curvature along the periphery of this layer, then we must have

$$\mathrm{K}+\frac{\mathrm{H}}{2}\left(\frac{1}{\rho}+\frac{1}{\rho_1}\right)=\mathrm{K}+\frac{\mathrm{H}}{2}\left(\frac{1}{\mathrm{R}}+\frac{1}{\mathrm{R}_1}\right)+\mathrm{D}(h-z).$$

For the normal pressure we may often use the right-hand side of the last equation, instead of the left. The terms under Σ arising from gravity have the form

$$\mathrm{D}\,z\,\mathrm{S}\,dz,$$

where S is the area of a section at the height z.

Therefore for the whole mass, if $d\mathrm{O}$ denotes an element of surface, we may write

$$\Sigma\,\tfrac{1}{2}m\mathrm{V}^2=\tfrac{1}{2}\int r\cos(\mathrm{N},r)\,d\mathrm{O}\left\{\mathrm{K}+\frac{\mathrm{H}}{2}\left(\frac{1}{\mathrm{R}}+\frac{1}{\mathrm{R}_1}\right)+\mathrm{D}(h-z)\right\}$$
$$+\tfrac{1}{2}\mathrm{D}\int z\,\mathrm{S}\,dz.$$

By the method given before there is no difficulty in determining

$$\int r\cos(\mathrm{N},r)\,d\mathrm{O}\left\{\mathrm{K}+\frac{\mathrm{H}}{2}\left(\frac{1}{\mathrm{R}}+\frac{1}{\mathrm{R}_1}\right)\right\},$$

when we consider that K, H, R, R_1 are constant. Its value is

$$3\left\{\mathrm{K}+\frac{\mathrm{H}}{2}\left(\frac{1}{\mathrm{R}}+\frac{1}{\mathrm{R}_1}\right)\right\}v,$$

where v is the volume.

It is also easy to see that

$$\int z\,\mathrm{S}\,dz=z_1v,$$

where z_1 is the height of the centre of gravity of the mass.

To investigate

$$\int r\cos(\mathrm{N},r)\,d\mathrm{O}\,(h-z)$$

we use Green's theorem,

$$\int\mathrm{G}\frac{d\mathrm{L}}{dn}\,d\mathrm{O}=\int\mathrm{G}\nabla^2\mathrm{L}\,dk+\int\frac{d\mathrm{G}}{dg}\,\frac{d\mathrm{L}}{dl}\cos\delta\,dk,$$

where G and L are functions of x, y, z, the left-hand integral is taken over the whole surface of a given closed space, and the integrals at the right-hand side are taken throughout that space.

$\dfrac{dL}{dn}$ is the differential coefficient of L along the normal to the closed space; and $\dfrac{dL}{dl}$, $\dfrac{dG}{dg}$ are the differential coefficients of L, G along the normals to the surfaces $L=C$ and $G=C'$; while δ is the angle between the last-named normals. We saw before that

$$r\cos(N, r)=\tfrac{1}{2}\frac{dr^2}{dn};$$

thus the integral becomes

$$\tfrac{1}{2}\int\frac{d(r^2)}{dn}(h-z)\,dO.$$

In Green's theorem, putting $h-z$ for G and r^2 for L, and noticing that

$$\nabla^2 r^2=6,\quad \frac{dG}{dg}=-1,\quad \frac{dL}{dl}=2r,\quad \cos\delta=\frac{z}{r},$$

we get

$$\tfrac{1}{2}\int\frac{d(r^2)}{dn}(h-z)dO=\tfrac{1}{2}\int 6(h-z)dk-\tfrac{1}{2}\int 2z\,dk.$$

Substituting this value, we get

$$\Sigma\,\tfrac{1}{2}mV^2=\tfrac{3}{2}v\left\{K+\frac{H}{2}\left(\frac{1}{R}+\frac{1}{R_1}\right)\right\}+\tfrac{3}{2}D\int(h-z)dk,$$

or

$$\Sigma\,\tfrac{1}{2}mV^2=\tfrac{3}{2}v\left\{K+\frac{H}{2}\left(\frac{1}{R}+\frac{1}{R_1}\right)+D(h-z_1)\right\},$$

where, as before, z_1 is the ordinate of the centre of gravity.

Thus, if ρ, ρ_1 are the principal radii of curvature at a point of the section through the centre of gravity, then

$$\Sigma\,\tfrac{1}{2}mV^2=\tfrac{3}{2}v\left\{K+\frac{H}{2}\left(\frac{1}{\rho}+\frac{1}{\rho_1}\right)\right\}\ldots\quad(\alpha)$$

Hence we see that the effect of gravity is of the same order as the molecular constant H, and conversely.

In proving the formula of Clausius (p. 338) we found generally that

$$\Sigma\,\tfrac{1}{2}mV_x^2=-\tfrac{1}{2}\Sigma\,Xx.$$

It might be thought, since gravity acts only in a vertical direction, that V_z^2 should be greater than V_x^2 or V_y^2. In a solid body this certainly is so. In a liquid, however, the equality of V_z^2 and V_x^2 follows from the supposition that a pressure experienced by any element is propagated equally in every direction.

There is still a difficulty to be overcome; and for that purpose we require to calculate the value of $\frac{1}{2}\Sigma mV_z^2$. Looking at it in another way, we may regard what follows as a more obvious kind of proof of equation (α). This simplification will have the advantage of affording us a more extended view of the subject. We consider, as before, that the forces acting on the system may be conveniently divided into two sets—one set acting on the surface only (with whose vertical components we are alone concerned), and the other acting throughout the mass of the liquid. The force acting on each element of surface is

$$dO\left\{K+\frac{H}{2}\left(\frac{1}{R}+\frac{1}{R_1}\right)+D(h-z)\right\}\cos(z, N);$$

so we get

$$\Sigma\,\tfrac{1}{2}mV_z^2=\tfrac{1}{2}\int z\,dO\cos(z, N)\left\{K+\frac{H}{2}\left(\frac{1}{R}+\frac{1}{R_1}\right)+D(h-z)\right\}$$
$$+\tfrac{1}{2}D\int z\,S\,dz.$$

Let dU be the projection of dO on the horizontal plane. This makes the right-hand side of the equation to depend on $\int z\,dU$ and $\int z^2dU$, the parts of the projection belonging to the under surface of the body being reckoned negative. Each element of $\int z\,dU$ represents an elementary cylinder; so that the value of this integral is equal to the volume of the liquid. We shall express an element of $\int z^2\,dU$ by $z^2\Delta U$. Let z_2 be the greatest ordinate of the element of surface whose projection is ΔU; and let z_3 be the shortest ordinate. Then $\int z^2dU$ may be taken as the limiting value of $\Sigma(z_2^2-z_3^2)\Delta U$. This is equal to $2\Sigma(z_2-z_3)\Delta U\left(\frac{z_2+z_3}{2}\right)$. But we may imagine the liquid to be divided into elementary cylinders, one of which is represented by $(z_2-z_3)\Delta U$; and this has its centre of gravity at a height $\frac{z_2+z_3}{2}$ above the horizontal plane. This leads to

$$\int z^2 dU = 2vz_1.$$

Substituting these values, we get

$$\tfrac{1}{2}\Sigma m V_z^2 = \tfrac{1}{2}v\left\{K + \frac{H}{2}\left(\frac{1}{\rho}+\frac{1}{\rho_1}\right)\right\},$$

or

$$\Sigma m V_z^2 = \tfrac{1}{3}\Sigma m V^2.$$

This result shows, as is easy to see, that in the case of liquids, just as in that of gases, no direction has any pre-eminence so far as the motions of the molecules are concerned; and that this is true whether the system is acted on by directed forces or not.

Chapter IV.

On the Potential Energy of a Liquid.

So long as there is any finite distance between two attracting particles, these must have a certain amount of potential energy. The amount can best be determined by calculating its increment resulting from the removal of one of the particles from a smaller to a greater distance. If there is a limit beyond which the molecules cannot approach each other, we must consider these as having potential energy even when they reach it, just as we consider a weight resting on a frictionless horizontal platform to have the same potential energy as if it were at the same height in free space. The same is also true in the case where the limit consists in the continuous motion of elastic bodies, as where a weight is supported by a piston above a confined mass of gas. Consequently it is true that weights have potential energy whether they be supported by surfaces or whether they are kept in equilibrium by bodies in motion. Similarly, we cannot say that a particle has no potential energy just because it happens to be in equilibrium. A particle inside a hollow spherical shell is in equilibrium if the attractive force between it and the material of which the shell is composed is subject to the law of the inverse square. There is no force on such a particle, and yet we cannot say that it has no potential energy with respect to the particles of the shell. Just in the same way an electrified particle placed within a hollow conductor is in equilibrium, but we are not justified in saying that it has no potential energy of electrification with respect to the shell. The fact is that in these last two cases the potential energy of the particle is not zero but constant; and if no forces act on it the cause is to be sought not in an absence of potential energy, but in the fact that the energy will be the same for all positions which it is free to assume. This is exactly the case of a molecule situated within the mass of a liquid. Here the molecule experiences no force because the potential energy is constant during displacement of the particles so long as they remain within the surface. This is a case of mutually attracting particles, between which, nevertheless, there are definite distances. It is the molecular motion which prevents the further approach of these particles, but it is not to be counted in finding their potential energy. If the approach of the molecules to one another were prevented by repulsive forces, the amount of potential energy could not be calculated without a knowledge of the laws of action of the forces and the distances apart of the molecules; but even here the potential energy would not be zero unless the two sets of forces followed the same law.

If we wish to calculate the potential energy of a number of attracting particles, we must first find its value for each separate particle, and the sum of these values will clearly give twice the potential energy of the system. For example, in calculating the potential energy of the particle *a*, we have brought in the particle *b*, and conversely for *b* we have brought *a* in; and thus have counted twice the quantity which ought to be taken only once. In other words we have to find the quantity which in the theory of electricity is termed the potential of a body on itself, and which is expressed analytically by $\frac{1}{2}\int \rho \, dk \, V$, where V is the value of the potential on a unit of mass occupying the elementary space dk throughout which the density is ρ.

We begin by establishing the value of the potential for a particle in the interior of a liquid. This value will clearly be the same for all the particles. Each of these particles can be considered to have lost potential energy with respect to the others lying within its sphere of action. As for the potential energy which it has with respect to those outside that sphere, no loss will have taken place, as these are practically at an infinite distance. Suppose the sphere of action to be cut into hemispheres, then we shall only have to find the loss of potential energy which each particle experiences in moving up from an infinite distance to its position specified with respect to this sphere. This, in consequence of our former research, is an easy matter. We know that the force experienced by a unit particle at a distance x from the plane surface of an attracting hemisphere is $2\pi D\psi(x)$; where D stands for the density of the attracting hemisphere.

The potential energy lost by an infinitely small motion of the particle through a distance dx, is of course $2\pi D\psi(x)dx$; and hence that lost altogether is

$$\int_0^\infty 2\pi D\psi(x)\,dx = \frac{K}{D};$$

and for the whole sphere of action $\frac{2K}{D}$.

If we could consider all the particles as bounded on all sides by liquid, then $\frac{1}{2}\int\rho\, dk\, V$ would simply become vK, where v is the volume of the liquid. This of course we cannot do for the boundary layers, but we could do it by coating the surface everywhere with a new layer of a thickness equal to the radius of the sphere of action. From this we see that the loss of potential energy is less in the external layer than it would have been had the coating taken place, and the amount of this deficiency is the work which would have been required to remove this coat had it ever been present. In order to determine what amount of work this is, we consider the energy expended in displacing an infinitely thin column from the surface of the liquid to infinity. For simplicity we will consider the liquid surface as plane, since any deviation from this condition will only introduce terms of the second order. Let an element of the cylinder of height dx be at a distance x from the surface. The force exerted by this particle on the mass is

$$2\pi\, D^2\, \psi\,(x)\, dx.$$

In order to carry it away through a distance dx, work is required to the extent of

$$2\pi\, D^2\, \psi(x)\, dx\, dx.$$

During this displacement another particle will come into the place just vacated by the one considered ; so that for the same value of x the work will be repeated as often as dx will divide x. In other words, to remove the column through an element of length requires $2\pi\ D^2 x\psi(x)dx$ of work, and to remove it through all the elements

$$2\pi D^2\int_0^\infty x\psi(x)dx = \text{H}.$$

So for the whole surface the work done is HO ; the potential energy lost is in consequence

$$\{v\text{K}-\tfrac{1}{2}\text{HO}\}.$$

If vC represents the quantity of potential energy which the mass would have were all the particles removed from the range of mutual action, then the quantity which actually exists is

$$\text{A} = \{v(\text{C}-\text{K}) + \tfrac{1}{2}\text{HO}\} \quad . \quad . \quad . \quad . \quad (\beta)$$

Equation (β) has many important consequences, some of which we shall shortly discuss. Evidently the potential energy tends towards a minimum. Now since v is determined by the molecular motion, it has a given value for a given temperature ; consequently the surface must be a minimum. Therefore a mass of liquid must take the form of a sphere, when only molecular forces act.

In order to increase the surface when the volume is given, an amount of work $\Delta\text{A} = \frac{1}{2}\text{H}\Delta\text{O}$ is necessary. This leads again to another signification of $\frac{1}{2}$H ; it represents the work in millimetre-milligrams necessary to increase the surface by one square millimetre. From its small value we see how small is the amount of work necessary to change the form of a liquid. The result that $\dfrac{\text{H}}{2}$ denotes the work as above quite agrees with the former view of $\frac{H}{2}$, where we took it equal to a tension of 8·2 mg. in a strip 1 mm. wide. Thus we see that to consider a liquid as being contained within a film of constant tension, the volume remaining unchanged, gives results which are continually confirmed.

However small the tension $\frac{H}{2}$ may be, it is yet the cause of a whole set of phenomena in the province of capillarity, not only of the elevation or depression of liquids in narrow tubes or between plates close together, but also of the form of resting or hanging drops, of bubbles in liquids, etc.; in short, of all that concerns the external form of a liquid. It is not within our province to go more closely into the important researches which have been made on this subject; not even into those of Plateau, Quincke, Van der Mensbrugghe, Lüdtge, and others. We will content ourselves by mentioning only the striking experiments lately made by Bosscha, which prove the presence of this tension even in cases where formerly it was not suspected *. Later we shall see that it exists not only in liquids but also in all so-called gases. The quantity which we have called the molecular pressure in the case of vapours, and which is to be added to the external pressure, is

$$2\pi\int_0^\infty \psi(x)dx.$$

If this has a finite value, then

$$2\pi\int_0^\infty x\psi(x)dx$$

must also be finite.

We may expect it to be very small in all bodies whose molecules are as far apart as those of gases; but, on the other hand, a body on which its effect is sensible may very easily yield to its influence on account of the great mobility of the particles. The observation of this phenomenon is rendered difficult by diffusion. It is clear from the researches of Bosscha that in tobacco smoke, and most probably also in

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* *Note.*—The Essay was written in 1873.

steam in the form of clouds, the molecular pressure is sufficiently great to cause the appearance of capillary phenomena*. These are not of course typical of true vapours ; still our investigation receives powerful support from these phenomena, since it is our object to establish that between the liquid and gaseous states there is nothing but a quantitative distinction.

Chapter V.

Influence of the Structure of Molecules.

Hitherto we have treated molecules as points of mass, and have thus been led to a simplification of our problem, which, however, does not in any way agree with the phenomena exhibited by matter. We must now, therefore, proceed to apply corrections to our theory in two different directions. In the first place, molecules must be considered not as mere points of mass, but as aggregates built up of atoms just as larger masses of matter are built up of molecules. Most probably the molecule must be considered as belonging to the solid condition of matter in order to enable us to carry our investigation further from this point of view. According to the most modern views of Chemistry, the position (*Stelle*) which an atom occupies in the molecule is of the most far-reaching importance as causing the phenomena of Isomerism ; and must in so far be determinate. As a consequence of this internal structure of molecules internal forces come into play, and these we have hitherto neglected in treating molecules as if they were merely points of mass. Furthermore, if we consider a molecule of the simplest possible form, that is as consisting of only one atom, it will possess a definite extension in space, and consequently the forces acting on it, due to the influence of other molecules, can no longer be considered as acting at one definite point; several corrections must therefore be applied to the simple formulæ already found.

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* [In addition to the appearances noted by Bosscha bearing on this point, I can add the following. In wet capillary tubes clouds have a meniscus just like mercury, and are depressed in the same way. This effect is especially noticeable in a U-tube which has one arm dry and the other wet.—*Note by the German Translator.*]

For this purpose let us develop the formula of Clausius for bodies whose molecules are composed of atoms. Meanwhile in calculating the forces acting between molecules we shall retain the supposition that for each particle internal to the mass the forces act at a single point. This is the treatment we have hitherto pursued, and it of course involves neglecting for the present the influence of the extension of these particles in space.

Let the coordinates of the centre of gravity of a molecule be a, b, c, at the instant considered, and the coordinates of one of its particles at the same moment

$$a+x_1; \quad b+y_1; \quad c+z_1.$$

Then in the equation

$$\Sigma\tfrac{1}{2}mV^2 = \tfrac{1}{4}\frac{d^2\Sigma mr^2}{dt^2} - \tfrac{1}{2}\Sigma(Xx+Yy+Zz),$$

we can introduce the value $\Sigma\mu r^2$ for each molecule from the following equations:

$$\Sigma\mu r^2 = \Sigma\mu(a+x_1)^2 + \Sigma\mu(b+y_1)^2 + \Sigma\mu(c+z_1)^2,$$

where μ represents the mass of an atom.

But from the definition of the centre of gravity

$$\Sigma\mu x_1 = 0, \quad \Sigma\mu y_1 = 0, \quad \Sigma\mu z_1 = 0;$$

so that for each molecule

$$\Sigma\mu r^2 = \Sigma\mu(a^2+b^2+c^2) + \Sigma\mu(x_1^2+y_1^2+z_1^2);$$

putting $a^2+b^2+c^2 = \rho^2$ and $x_1^2+y_1^2+z_1^2 = r_1^2$,

we get $\Sigma\mu r^2 = m\rho^2 + \Sigma\mu r_1^2$,

where r_1 is the distance of the particle of mass μ from the centre of gravity.

The expression $\frac{d^2\Sigma mr^2}{dt^2}$ becomes in consequence

$$\frac{d^2\Sigma m\rho^2}{dt^2} + \frac{d^2\Sigma\mu r_1^2}{dt^2}.$$

$\Sigma m\rho^2$ is that quantity which we have already considered and represented by Σmr^2 while treating molecules as if they were mere particles. For the mean values of V, X, Y, Z, it may be considered as independent of the time. In the case where the temperature of the gas and therefore the distances of the atoms from the centres of gravity of the molecules can be considered constant—at all events in the mean—the second term $\Sigma\Sigma\mu r_1^2$ may be omitted. We may even regard the molecules themselves as continually altering, making the supposition that the alteration does not take place continuously in one direction. We must consider them as having, after some short period of time, returned to their previous configuration. So in this case also

$$\Sigma\tfrac{1}{2}m\mathrm{V}^2 = -\tfrac{1}{2}\Sigma(\mathrm{X}x + \mathrm{Y}y + \mathrm{Z}z).$$

Internal forces are the only ones concerned in holding the molecule together. Let f' be the force acting between two atoms of the molecule, ρ_1 the distance between these atoms, let the external pressure be N, the molecular pressure N_1, the volume v; then the equation becomes

$$\Sigma\tfrac{1}{2}m\mathrm{V}^2 = \tfrac{1}{2}\Sigma\Sigma f'\rho_1 + \tfrac{3}{2}(\mathrm{N} + \mathrm{N}_1)v.$$

If we omit the term $\tfrac{1}{2}\Sigma\Sigma f'\rho_1$ neglecting the forces which hold the molecule together, the quantity of kinetic energy thus calculated will be found too small. If we also omit N_1 we obtain our former equation, $\Sigma\tfrac{1}{2}m\mathrm{V}_1^2 = \tfrac{3}{2}\mathrm{N}v$.

We can now see clearly what it is that V_1 denotes in the last equation. By neglecting the forces acting between the parts of a molecule we do not alter the motion of its centre of gravity. Thus V_1 is the mean value of the velocities of the centres of gravity of the molecules, or, as Clausius calls it, the Velocity of Progressive Motion.

To compute this velocity, let us write the last equation in the form previously given (p. 341),

$$\mathrm{V}_1^2 = 3\mathrm{N}\frac{g}{\delta_0}(1+at).$$

For atmospheric air, $\mathrm{N} = 10334$ kilograms, and $\delta_0 = 1{\cdot}293$. Hence for a gas of density δ,

$$\mathrm{V}_1^2 = \frac{3 \times 10334 \times 9{\cdot}812}{1{\cdot}293} \times \frac{1+at}{\delta},$$

or $$\mathrm{V}_1 = 485\sqrt{\frac{1+at}{\delta}} \text{ metres per second.}$$

If by heating a gas the velocity of progressive motion alone is increased, the specific heat will be given by the equation

$$d(\tfrac{1}{2}mV_1^2) = \tfrac{3}{2}d(Nv) = Ac_0dt,$$

where A is the mechanical equivalent of heat.

Assuming that Nv is proportional to the absolute temperature, we have $d(Nv) = Rdt$. Here $R = \frac{1}{273}$ of the product got by multiplying N (in kilograms per square metre) by v (the volume in cubic metres of the unit of weight of the gas at 0° C.). For air, $R = 29{\cdot}272$. Therefore $c_0 = \frac{3}{2} \times \frac{29{\cdot}272}{424}$ $= 0{\cdot}1035$ unit of heat (Centigrade-kilograms).

For other gases,

$$c_0 = \frac{0{\cdot}1035}{\delta};$$

or since $\frac{1}{\delta} = vd_0$, where d_0 is the density of air and v is the volume of one kilogram of the gas, we have

$$c_0 = 0{\cdot}1035\, vd_0$$

or

$$\frac{c_0}{v} = 0{\cdot}1035\, d_0.$$

This equation shows that for unit volume the specific heat required to increase the velocity of progressive motion is constant.

That 0·1035 unit of heat is too small a number, if we are to understand by it the whole specific heat of air, appears from two experimental data: namely, the specific heat for constant pressure, and its ratio to that at constant volume. Regnault found the first to be 0·2375; and from the velocity of sound, among other data, the specific heat for constant volume is by calculation 0·1685.

The value 0·1035 could not be right unless we considered $\Sigma\Sigma\frac{1}{2}f'\rho_1$ to be zero. Since f' denotes the force mutually exerted by the atoms in the molecule, and this cannot be zero, we can foresee a difference between the calculated value and the value given by experiment. Opinions differ as to the cause of this difference. Two suppositions have been more or less fully developed.

Thus Clausius says:—"We must arrive at the conclusion that besides the progressive motion of the molecule as a whole, there are other motions of its constituent parts the kinetic energy of which is equivalent to part of the heat." While Clausius ascribes the difference to an increased motion of the atoms, others ascribe it to a motion of rotation of the molecule associated with the progressive motion. In fact it is only in exceptional cases that a normal impulse on a body which is not spherical will produce a motion of pure translation. The second supposition has been investigated by Maxwell. He calculates that in a system of solid elastic bodies of any form moving in a given space and continually colliding, the kinetic energy is divided between energy of rotation and energy of translation; and, further, that the kinetic energy due to rotation is equal to the kinetic energy due to translation. But since this equality does not exist in any gas, he goes on to say that we cannot regard the molecules as rigid, perfectly elastic, non-spherical bodies. Probably no one professes to hold this view, at least for molecules consisting of several atoms. Inasmuch as a molecule is built up of several atoms, we cannot regard it as rigid. Can we even ascribe elasticity to it? If during the impact of two bodies no energy of motion of the bodies as a whole is converted into energy of relative motion of their parts, we may, for our present purpose, term these bodies perfectly elastic. This condition is approximately fulfilled by two ivory balls. Now it is not certain *à priori* that molecules do fulfil the required condition; and therefore we are not justified in assuming them to be endowed with the property (thus defined) of perfect elasticity. It is quite possible that part of the kinetic energy of motion of the molecule is converted into kinetic energy of relative motion of its parts. Increase of temperature, which is at first identified with increase of the progressive motion, is followed by increase of the internal motion of the molecules. Consequently it is only for constant temperature that we shall be justified in discussing elasticity as defined above.

As before let V_1 be the velocity of progressive motion, then by a previous relation

$$d(\tfrac{1}{2}m\mathrm{V}_1^2)=\tfrac{3}{2}d(\mathrm{N}v)=\tfrac{3}{2}\mathrm{R}dt=\mathrm{A}c_0dt. \quad . \quad . \quad . \quad (1)$$

Now if V denotes a velocity which, if possessed by the molecule, would correspond to its whole actual kinetic energy, and if c_1 be the specific heat for constant volume, we have

$$d(\tfrac{1}{2}m\mathrm{V}^2)=d\Sigma\tfrac{1}{2}f'\rho_1+\mathrm{A}c_0dt=\mathrm{A}c_1dt. \quad . \quad . \quad . \quad (2)$$

Further, c being the specific heat for constant pressure, we have

$$d(\tfrac{1}{2}m\mathrm{V}^2)+\mathrm{N}dv=\mathrm{A}cdt. \quad . \quad . \quad . \quad . \quad (3)$$

Moreover, from $\mathrm{N}v=\mathrm{RT}$, we have for constant pressure

$$\mathrm{N}dv=\mathrm{R}dt, \text{ or } \mathrm{N}dv=\tfrac{2}{3}\mathrm{A}c_0dt.$$

Substituting in (3) this value for $\mathrm{N}dv$, and for $d(\frac{1}{2}m\mathrm{V}^2)$ the value given by (2), we arrive at the equation given by Clausius,

$$\mathrm{A}c_1dt+\tfrac{2}{3}\mathrm{A}c_0dt=\mathrm{A}cdt\,;$$

or

$$c_0=\tfrac{3}{2}(c-c_1),$$

or

$$\frac{d(\frac{1}{2}m\mathrm{V}_1^2)}{d(\frac{1}{2}m\mathrm{V}^2)}=\tfrac{3}{2}\left(\frac{c}{c_1}-1\right).$$

For gases the molecules of which consist of two atoms, $\frac{c}{c_1}$ is equal to 1·421; and the ratio we are looking for, that is of c_0 to c_1, is 0·6315.

This, however, only gives the value of the ratio, without showing the cause of the phenomenon. Equation (2) shows that the difference between c_0 and c_1 must be ascribed to a change of condition of the molecules. The signification of $d\frac{1}{2}\Sigma\Sigma f'\rho_1$ must be that the attracting atoms alter their distances when the heat increases.

Putting $\mathrm{V}^2-\mathrm{V}_1^2=\mathrm{V}_0^2$ we get

$$\Sigma\tfrac{1}{2}m\mathrm{V}_0^2=\tfrac{1}{2}\Sigma\Sigma f'\rho_1.$$

Remembering that this result was arrived at by putting $\frac{d^2(\Sigma\Sigma\mu r_1^2)}{dt^2}$ equal to zero, we evidently cannot suppose $\frac{1}{2}m\mathrm{V}_0^2=\frac{1}{2}\Sigma f'\rho_1$ for each molecule at every instant. By doing so we should tacitly assume the invariability of the molecule.

If we do put $\frac{1}{2}m\mathrm{V}_0^2=\frac{1}{2}\Sigma f'\rho_1$, then the law of force between the atoms can be deduced. In the case of a molecule of two atoms we can easily find the path described by each atom round their common centre of gravity.

In this case $m=2\mu$ and $\rho_1=2r_1$, where μ is the mass of an atom, and r_1 is the distance of each atom from their common centre of gravity.

The equation may be written $\frac{\mu V^2}{r_1}=f$,

where f is the central force on each atom towards the point about which it moves. To determine the path we need only use the known relations for central forces. We get by integration $r\frac{dr}{dt}=$constant. The path is a logarithmic spiral, and the force is inversely proportional to the cube of the distance of the atom from the centre of the molecule. This result would contradict our first supposition that $\frac{d^2(mr^2)}{dt^2}=0$. It is only in the particular case of circular motion, when the above constant happens to be zero, that we obtain a result consistent with $\frac{d^2(mr^2)}{dt^2}$ being equal to zero.

Retaining the term $\frac{d^2(mr^2)}{dt^2}$ we get

$$\mu V^2=\tfrac{1}{2}\mu\frac{d^2(r^2)}{dt^2}+fr,$$

or

$$\frac{f}{\mu}=r\left(\frac{d\theta}{dt}\right)^2-\frac{d^2r}{dt^2},$$

which accords with a well-known expression for a central force.

In other words, this equation only shows that each atom describes some path about the centre of gravity, but does not in any way determine the form of path, because the law of force is unknown. It is most probable that the path is curved, and is not a path of rectilinear vibration. But we thus see that the two apparently different suppositions made to account for the part of the kinetic energy, which is not accounted for by the progressive motion, really agree. We may, with Clausius, consider this to exist either in the relative motion of the constituent atoms, or we may look for it in motion of rotation.

Now Maxwell considers the problem of a small body rotating about an axis, and his treatment introduces into the calculation the moments of inertia of this body about three principal axes. We see that this method of regarding a molecule probably does not sufficiently meet the case. As a preliminary hypothesis, we may regard the atoms as points having mass, and for the moment of inertia of the molecule we may take the sum of the products of the masses into the squares of the distance of each atom from the centre of gravity.

Chapter VI.

Influence of the Extension of the Molecule.

We arrived at the conclusion that if the kinetic energy of the progressive motion is denoted by $\Sigma\frac{1}{2}mV^2$, then the equation

$$\Sigma\tfrac{1}{2}mV^2=\tfrac{3}{2}(N+N_1)v$$

may properly be admitted. Further on we shall see by application to carbonic acid and other gases that the equation still holds for these, even in the so-called liquid state, provided a correction is introduced for the extension of the molecules. In the left-hand side of the equation only the motion of the molecule as a whole is included; similarly on the right-hand side the moments of the forces which keep the atoms together are omitted.

In order to find the correction arising from the size of the molecules, I have thought it well to adopt a method different from that hitherto pursued. Of course the effect of the extension will be to make the volume within which the motion takes place smaller than it seems to be. At first I considered that the difference between the external volume and the volume taken up by the molecules was the space within which the motion takes place. But I trust to be able to prove, by further considerations, that up to a certain degree of condensation of matter the external volume must be diminished by four times the volume of the molecules, and for greater condensation that it must be diminished by a continuously diminishing multiple of this volume. We no longer then regard the molecules as centres of force without extension, though this supposition was allowable at first as a rough approximation. Researches on the diffusion and viscosity of gases have shown that we ought rather to view molecules as small extended bodies, and the following results of mine will confirm the truth of this view.

Clausius and Maxwell have calculated the mean free path of the molecules. If, however, their method is closely considered it appears that they give the molecules extension in a plane perpendicular to the direction of motion, but none in the direction of this motion; we may say that they give them breadth but no thickness. The simplification introduced by them amounted to neglecting the thickness of the molecules compared with the mean free path. Consequently they have made the mean path too great; just as if the free path of a ball thrown against a wall were said to be the distance of the centre of the ball from the wall when the motion began; whereas the free path is that distance minus the radius of the ball. Thus considering the diameter of the molecule we get a shorter free path, and consequently a proportionately greater number of encounters. But then the opposing pressure must be greater in proportion. We know from previous work that the pressure can be calculated from a knowledge of the fact that it is proportional to the number of impulses of molecules on the unit of surface in unit time, the mass and velocity of the molecules being given.

Let us first seek an expression for the mean free path on the simpler supposition. Let V be the velocity of a moving molecule, the others being supposed at rest; let n be the number of molecules in unit volume. Then in one second the moving molecule will get within a distance s of $V\pi s^2 n$ other molecules. This is the number which would be contained within a cylinder whose axis is parallel to the direction of motion and numerically equal to V, and whose base is πs^2. If there are any molecules against which the moving one impinges, the direction of the path will be changed; but since these molecules are to have no thickness, the number approached within a distance s remains the same. We thus get different cylindrical pieces which could be made up into a cylinder of the above size. If s is the distance between the centres of the molecules when an encounter takes place, then $V\pi s^2 n$ will be the number of impulses in a second; and if l is the mean path between two impulses, then $V\pi s^2 nl$ is the distance traversed in one second, and is therefore equal to V. Hence

$$l = \frac{1}{\pi s^2 n}.$$

Let λ be the mean distance of the molecules supposed to be arranged in cubical order, then $n\lambda^3$ is the volume taken above as unit. Hence

$$l = \frac{\lambda^3}{\pi s^2}.$$

So far only one molecule is supposed to move, the others being at rest. Clausius has shown that if all the molecules move, the mean path is $\frac{3}{4}$ths of that just found; that is

$$l_1 = \frac{\lambda^3}{\frac{4}{3}\pi s^2}.$$

So far we have followed Clausius. We must now find how much the diameter of the molecules diminishes the path. If all the impulses were in the direction joining the centres of the molecules considered as spheres, then l_1 would have to be diminished by the distance between the centres when impact occurs. For half the diameter of the molecule must be subtracted at the beginning as well as at the end of the free path. Thus

$$l_2 = l_1 - s \text{ or } \frac{\lambda^3 - \frac{4}{3}\pi s^3}{\frac{4}{3}\pi s^2},$$

or

$$\frac{l_2}{l_1} = \frac{\lambda^3 - \frac{4}{3}\pi s^3}{\lambda^3}.$$

Considering that $\frac{1}{2}s$ is the radius of the molecule here regarded as a sphere, and that $n\lambda^3$ is equal to the unit volume here taken as v; also that $\frac{4}{3}\pi ns^3$ is eight times the volume of the molecules themselves; we get

$$\frac{l_2}{l_1} = \frac{v - 8b_1}{v},$$

where b_1 is the volume of the molecules.

The encounters, however, are only central exceptionally; and therefore, in the mean, l_1 must be diminished by less than s. From the following considerations we can find what fraction of s is to be subtracted from l_1. At the instant of impact the centre of the moving molecule lies on a sphere of radius s described about the centre of the second molecule. Consider this sphere bisected by a plane perpendicular to the direction of motion. For central impact the centre of the moving molecule has its greatest distance from this plane, for grazing impact the centre is in this plane, and for intermediate cases the centre is at other points of the hemispherical surface. The diminution of the path is the distance at impact of the centre of the moving molecule from the plane, and hence the mean diminution of the mean path is the mean ordinate of the hemisphere. But since the centre is equally likely to fall on any point of the hemisphere, we must take the mean ordinate for equal elements of the hemispherical surface, and not, as might easily be thought, for equal elements of the plane. We have to find

$$\frac{\int z d\omega}{\int d\omega},$$

where $d\omega$ is an element of surface. This is the ordinate of the centre of gravity of a hemispherical surface, and is known to be half the radius. Hence from l_1 we must subtract $\frac{1}{2}s$ and not s. Putting $l_1 - \frac{1}{2}s = l_3$, we get

$$\frac{l_3}{l_1} = \frac{v - 4b_1}{v}.$$

This relation can be more rigidly proved by the following considerations*:—

If $f(x)dx$ denotes that fraction of the molecules in a given volume whose velocity component parallel to the axis of x is between the values x and $x + dx$, then we must have (Maxwell, Phil. Mag. [4] xix. p. 19) :—

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* [This is contained in a later discussion by the Author, *Archives Néerl.* xii. pp. 200-216 (1877) :—“ On the relative number of impacts experienced by a molecule moving among molecules at rest, and among molecules in motion; and on the influence exerted by the size of the molecule (in the direction of relative motion) on the number of these impacts.” We have

$$\int_{-\infty}^{\infty} f(x)dx=1.$$

If n is the total number of molecules, then the number of molecules the velocity of which has components between x and $x+dx$, y and $y+dy$, z and $z+dz$ respectively is

$$nf(x)f(y)f(z)\,dx\,dy\,dz^{*}.$$

If these molecules start from the origin at the same time, then at the end of one second they will lie within the element of space $dx\,dy\,dz$ near the point P, whose coordinates are x,y,z. If P is on the axis of x at a distance r from the origin, the factor of $dx\,dy\,dz$ is $nf(r)f(0)^2$.

If P is anywhere at distance r the factor must have the same value, since the law of the velocities is the same in all directions.

Hence

$$f(x)f(y)f(z)=f(\sqrt{x^2+y^2+z^2})\,.f(0)^2\,;$$

consequently

$$f(x)^3=f(0)^2f(x\sqrt{3}). \quad . \quad . \quad . \quad . \quad . \quad (\text{I.})$$

If P is in the plane of xy, then

$$f(x)f(y)f(0)=f(0)^2f(\sqrt{x^2+y^2+z^2}),$$

or

$$f(x)^2=f(0)f(x\sqrt{2}). \quad . \quad . \quad . \quad . \quad . \quad (\text{II.})$$

First let us find what function satisfies (I.). Denote $\log f(x)$ by $\phi(x)$, then from equation (I.) we get

$$3\phi(x)=2\phi(0)+\phi(x\sqrt{3}),$$

$$3\phi'(x)=\sqrt{3}\phi'(x\sqrt{3}),$$

$$\phi''(x)=\phi''(x\sqrt{3}). \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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not thought it permissible to suppress completely the above not unobjectionable proof, in order—as far as possible—to exhibit in a connected form the earlier methods of treatment of the Author. The following references may be given:—Korteweg, *Arch. Néerl.* xii. p. 254 (1877); Clausius, Pogg. *Ann.* cv. p. 239 (1858), cxv. p. 20 (1862), Ergbd. vii. p. 215 (1876), and Wied. *Ann.* x. p. 92 (1880).—*Note by German Translator.*]

* The proof of this is given in Boltzmann, *Studien über das Wärmegleichgewicht* &c.

Constructing a curve whose abscissæ are the values of $\log x$ and ordinates the values of $\phi''(x)$, then by (1) this curve must represent a periodic function whose period is $\frac{1}{2}\log 3$.

Similarly from (II.) we get

$$\phi''(x)=\phi''(x\sqrt{2}), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

so that the above curve, in addition to the period $\frac{1}{2}\log 3$, must have the period $\frac{1}{2}\log 2$. This would be a contradiction unless the curve be a straight line parallel to the axis of x; in other words $\phi''(x)$ must be constant.

Hence we easily get

$$f(x)=\mathrm{C}e^{-\frac{x^2}{\alpha^2}},$$

where x^2 is affected with the minus sign because the function must diminish when x increases. The meaning of α, which is introduced for the sake of homogeneity, will appear later. From

$$\int_{-\infty}^{\infty} f(x)dx=1, \text{ follows } \mathrm{C}=\frac{1}{\alpha\sqrt{\pi}}.$$

By help of this we easily find the law of the velocities among the above number of molecules near the point P. In fact this number $nf(x)f(y)f(z)\,dx\,dy\,dz$ is equal to

$$\frac{n}{\alpha^3\pi\sqrt{\pi}}e^{-\frac{r^2}{\alpha^2}}r^2dr\sin\phi\,d\phi\,d\theta,$$

using polar coordinates in which ϕ is the angle between the radius vector to P and the axis of z, and θ is the angle made by the projection of the radius vector on the plane of xy, and the axis of x. This expresses the number of molecules which started from the origin at the same instant in the direction (ϕ, θ), and after the expiration of one second lie between the distances r and $r+dr$. Integrating between $\theta=0$ and $\theta=2\pi$, we get

$$\frac{2n}{\alpha^3\sqrt{\pi}}e^{-\frac{r^2}{\alpha^2}}r^2dr\sin\phi\,d\phi$$

for the number which arrive at a distance between r and

$r+dr$ inclined at an angle ϕ to the axis of z. Integrating again between $\phi=0$ and $\phi=\pi$, we get

$$\frac{4n}{\alpha^3\sqrt{\pi}}e^{-\frac{r^2}{\alpha^2}}r^2dr$$

for the total number whose velocities are between r and $r+dr$. Here all the velocities are to be considered positive (being along r), hence

$$\int_0^\infty \frac{4}{\alpha^3\sqrt{\pi}}e^{-\frac{r^2}{\alpha^2}}r^2dr=1.$$

$r^2e^{-\frac{r^2}{\alpha^2}}$ is a maximum for $r=\alpha$, thus α denotes the velocity most frequently occurring. For $r=0$ and $r=\infty$, we have $r^2e^{-\frac{r^2}{\alpha^2}}=0$.

The mean velocity, written in the form

$$\frac{4\alpha}{\sqrt{\pi}}\int_0^\infty \frac{r^2}{\alpha^2}e^{-\frac{r^2}{\alpha^2}}\frac{dr}{\alpha}\cdot\frac{r}{\alpha},$$

is found to be $\frac{2\alpha}{\sqrt{\pi}}$. The mean value of the square of the velocity is

$$\frac{4\alpha^2}{\sqrt{\pi}}\int_0^\infty \frac{r^4}{\alpha^4}e^{-\frac{r^2}{\alpha^2}}\frac{dr}{\alpha}$$

or $\frac{3}{2}\alpha^2$. The total kinetic energy is $\frac{3}{4}\alpha^2\Sigma m$. Writing $\frac{3}{4}\alpha^2\Sigma m=\frac{1}{2}V^2\Sigma m$, where, as with Clausius, V denotes the velocity which, if common to all the molecules, would give the same kinetic energy as they really possess, then $\alpha=V\sqrt{\frac{2}{3}}$.

For example, in the case of oxygen, for which Clausius gives $V=461$ metres per second, we find the most frequently occurring velocity to be 376, and the mean velocity $\frac{2\alpha}{\sqrt{\pi}}$ to be 425.

We now investigate for the assumed mean velocity the number of encounters experienced during one second, neglecting the size of the molecules in the direction of their motion: we do this for the three following cases:—

(*a*) One molecule alone moves, the others being at rest;
(*b*) One molecule is at rest, the others being in motion;
(*c*) A molecule moves among others which move.

For case (*a*) it appears from the considerations on p. 374 that the number of encounters is

$$\mathrm{N}=n\pi s^2\left(\frac{2\alpha}{\sqrt{\pi}}\right).$$

For case (*b*) describe tangential cylinders in all directions round a sphere whose radius is double the radius of the molecule. First let us find the number of encounters experienced by the molecules whose velocity is between v and $v+dv$. The number of these is

$$\frac{4n}{\sqrt{\pi}}\frac{v^2}{\alpha^2}e^{-\frac{v^2}{\alpha^2}}\frac{dv}{\alpha}.$$

The fraction of these whose direction of motion is parallel to the axis of the cylinder is $\frac{\sin\phi\,d\phi\,d\theta}{4\pi}$, and we may consider this motion as directed against the molecule at rest. If such a cylinder, whose base is πs^2, has a height vdt, then all the molecules within this cylinder which move parallel to the axis will reach the molecule which is at rest during the time dt. The number of these molecules is

$$n\pi s^2\,vdt\frac{4}{\sqrt{\pi}}\frac{v^2}{\alpha^2}e^{-\frac{v^2}{\alpha^2}}\frac{dv}{\alpha}\frac{\sin\phi\,d\phi}{2}\cdot\frac{d\theta}{2\pi}.$$

Hence for the total number we get $n\pi s^2\frac{2\alpha}{\sqrt{\pi}}$, the same as in case (*a*); so that these cases may be considered equivalent.

Case (*c*) is reduced to (*b*) by considering the motion of the other molecules relative to the one under consideration.

Let v be the velocity of this molecule, u the velocity of the others; and consider this last relatively to the molecule in question. If ϕ is the angle between the directions of u and v, then the relative velocity is

$$\sqrt{v^2+u^2+2uv\cos\phi}\,;$$

and we may regard the first molecule as at rest if we suppose the others to have this velocity. Proceeding as in case (*b*) we get

$$n\pi s^2\frac{4}{\sqrt{\pi}}\int_0^\infty\frac{u^2}{\alpha^2}e^{-\frac{u^2}{\alpha^2}}\frac{du}{\alpha}\int_0^\pi\sqrt{v^2+u^2+2uv\cos\phi}\,\frac{\sin\phi\,d\phi}{2}\int_0^{2\pi}\frac{d\theta}{2\pi}$$

for the number of encounters experienced in one second by the molecule whose velocity is v.

The value of

$$\int_0^\pi \sqrt{v^2+u^2+2vu\cos\phi}\,\frac{\sin\phi d\phi}{2}$$

is different according as $u<v$ or $>v$*.

In the first case $u<v$, the value is $v+\frac{u^2}{3v}$; when $u>v$ the value is $u+\frac{v^2}{3u}$. Hence the above integral divides into two parts, and becomes

$$n\pi s^2\frac{4}{\sqrt{\pi}}\left\{\int_0^v \frac{u^2}{\alpha^2}e^{-\frac{u^2}{\alpha^2}}\frac{du}{\alpha}\left(v+\frac{u^2}{3v}\right)+\int_v^\infty \frac{u^2}{\alpha^2}e^{-\frac{u^2}{\alpha^2}}\frac{du}{\alpha}\left(u+\frac{v^2}{3u}\right)\right\}.$$

And hence the mean value of the number of encounters experienced by a molecule in one second is

$$\mathrm{N}=n\pi s^2\frac{4}{\sqrt{\pi}}\frac{4}{\sqrt{\pi}}\int_0^\infty \frac{v^2}{\alpha^2}e^{-\frac{v^2}{\alpha^2}}\frac{dv}{\alpha}\left\{\int_0^v \frac{u^2}{\alpha^2}e^{-\frac{u^2}{\alpha^2}}\frac{du}{\alpha}\left(v+\frac{u^2}{3v}\right)\right.$$
$$\left.+\int_v^\infty \frac{u^2}{\alpha^2}e^{-\frac{u^2}{\alpha^2}}\frac{du}{\alpha}\left(u+\frac{v^2}{3u}\right)\right\}.$$

The values of these integrals are found as follows. On two rectangular axes take u, v as coordinates, and consider one part of the integral, for example

$$\int_0^\infty\int_v^\infty \frac{v^2}{\alpha^2}e^{-\frac{v^2}{\alpha^2}}\frac{dv}{\alpha}\frac{u^2}{\alpha^2}e^{-\frac{u^2}{\alpha^2}}\frac{du}{\alpha}\left(u+\frac{v^2}{3u}\right).$$

This expresses the volume between the plane of uv and a surface whose ordinate is the factor which multiplies $du\,.\,dv$ under the sign of the double integral. Since the limits of u are ∞ and v, this integration is over the part of the plane of $u\ v$ between the axis of u and the bisector of the angle between the axes of u and v. And the limits of v being 0 and ∞ show that the integration is to be extended over the whole of the eighth part of the plane of uv. Using polar coordinates $u=r\cos\psi$, $v=r\sin\psi$ the volume under consideration becomes

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* [This integral represents the mean length of lines drawn from a fixed point of a sphere to the points of a concentric sphere. The mean value is the same whether the fixed point be on the outer or the inner sphere. If R be the radius of the outer sphere and r the radius of the inner sphere, the mean value is $\mathrm{R}+\frac{r^2}{3\mathrm{R}}$.]

$$\alpha\int_0^\infty\int_0^{4}\frac{r^6}{\alpha^6}\frac{dr}{\alpha}e^{-\frac{r^2}{\alpha^2}}(\sin^2\psi-\tfrac{2}{3}\sin^4\psi)\cos\psi d\psi.$$

Similarly the other part of the integral becomes

$$\alpha\int_0^\infty\int_{\frac{\pi}{4}}^{\frac{\pi}{2}}\frac{r^6}{\alpha^6}\frac{dr}{\alpha}e^{-\frac{r^2}{\alpha^2}}(\cos^2\psi-\tfrac{2}{3}\cos^4\psi)\sin\psi d\psi.$$

Here the limits of u being 0 and v the integration is over the second half of the quadrant.

Putting $\psi=\frac{\pi}{2}-\psi'$, the last integral becomes

$$\alpha\int_0^\infty\int_0^{\frac{\pi}{4}}e^{-\frac{r^2}{\alpha^2}}\frac{r^6}{\alpha^6}\frac{dr}{\alpha}(\sin^2\psi'-\tfrac{2}{3}\sin^4\psi')\cos\psi' d\psi',$$

so that the two parts of N are equal.

Each of these integrals is $\frac{\sqrt{\pi}\sqrt{2}}{16}$, so that

$$\mathrm{N}=n\pi s^2\frac{2\alpha\sqrt{2}}{\sqrt{\pi}}.$$

Comparing this result with that obtained in cases (a) and (b) we find $\sqrt{2}$ to be the value, already put forward by Maxwell, for the ratio of the encounters under the hypotheses considered.

Although this coefficient (which by multiplication with the result of (a) or (b) produces a result equal to that deduced for (c)) is considerably greater according to Maxwell than it is according to Clausius, yet the number of impacts on Maxwell's theory is less than the number found by Clausius. This at least must be the case if Maxwell takes his mean value of v as that resulting from the mean value of the kinetic energy. In fact we get according to Maxwell the above value for N, and since we determined α to be $\mathrm{V}\sqrt{\frac{2}{3}}$, where V denotes the velocity taken by Clausius, it follows that

$$\mathrm{N}=n\pi s^2\tfrac{4}{3}\mathrm{V}\sqrt{\frac{3}{\pi}}.$$

But $\sqrt{\frac{3}{\pi}}$ is ·979. So that the value of N just obtained is ·979 of that which we should get on the assumption that all the molecules had the same velocity as that deduced from the mean kinetic energy. The factor changes in this case from $\sqrt{2}$ to $\frac{4}{3}$, which is Clausius' factor.

The difference of factors will become especially important when we treat of the mean path traversed by a molecule between two consecutive encounters. Following Clausius we found above (p. 374) that the mean free path l_1 was given by

$$l_1 = \frac{1}{n\pi s^2 \frac{4}{3}},$$

and now instead of this we must write

$$l_1 = \frac{1}{n\pi s^2 \sqrt{2}}.$$

This still leaves us to estimate the effects of the molecular dimensions in the direction of the relative motion. We have found that in case (*c*) a molecule moving with velocity v, and exposed to the action of molecules having velocities between u and $u+du$, and directions given by (ϕ, θ) with respect to v, suffers a number of impulses in each second given by

$$\frac{4\pi n s^2 u^2}{\sqrt{\pi\alpha^2}} e^{-\frac{u^2}{\alpha^2}} \frac{du}{\alpha} \sqrt{v^2+u^2+2uv\cos\phi}\, \frac{\sin\phi d\phi}{2} \frac{d\theta}{2\pi}.$$

This number is calculated on the assumption that the diameter of the molecule is to be neglected. In order to find the effect of the diameter it will be convenient to calculate what fraction of a second is required for the same number of encounters when the diameter is taken into account. For this purpose we must determine the shortening of the relative path incident on the extension of the molecules. Consider a molecule at rest; we have above defined the epoch of impact as that epoch at which the molecule in motion is the projection on the line of relative motion of the molecule at rest; in other words it is that moment when the centre of the moving molecule reaches a plane which is central and perpendicular to the relative motion. The shortening of the relative path must be represented by one or other of the ordinates of the concentric sphere of radius double that of the molecule, such ordinate being perpendicular to the plane as above defined. The mean value of this shortening is $\frac{2}{3}s$, a quantity which is derived from the volume of the hemisphere on the assumption that the probability of impact of a molecule at any given point of the central plane is the same for all points of the plane. Thus $\frac{2}{3}s$ represents the shortening of the relative path. So from the path of the striking molecule we must subtract a fraction

$$\frac{u}{\sqrt{u^2+v^2+2uv\cos\phi}}$$

of this, and from that of the molecule struck another fraction

$$\frac{v}{\sqrt{v^2+u^2+2uv\cos\phi}}$$

of the same quantity. So that for each encounter suffered by the latter the mean free path of the striking molecule will be shortened by

$$\tfrac{2}{3}s\frac{u}{\sqrt{v^2+u^2+2uv\cos\phi}}.$$

Summing this for all the encounters we obtain the integral

$$\tfrac{2}{3}s\pi n s^2\frac{4\alpha}{\sqrt{\pi}}\int_0^\infty \frac{u^3}{\alpha^3}e^{-\frac{u^2}{\alpha^2}}\frac{du}{\alpha}\int_0^\pi\frac{\sin\phi d\phi}{2}\int_0^{2\pi}\frac{d\theta}{2\pi},$$

which comes to

$$\tfrac{2}{3}n\pi s^3\left(\frac{2\alpha}{\sqrt{\pi}}\right).$$

Since this is independent of the velocity v it holds for all molecules. Therefore we get the same result on calculating for the molecule which we have hitherto considered at rest the amount by which its path (during one second) must be diminished so that it may experience the same number of encounters

$$n\pi s^2\frac{2\alpha\sqrt{2}}{\sqrt{\pi}}.$$

Now before we took the diameter into account we found that the length of the path travelled per second was $\frac{2\alpha}{\sqrt{\pi}}$; and this will now become

$$\frac{2\alpha}{\sqrt{\pi}}-\tfrac{2}{3}n\pi s^3\frac{2\alpha}{\sqrt{\pi}}.$$

The reciprocal of the ratio of these two paths will give the ratio of the number of encounters experienced in the same time on the two suppositions. This is

$$\frac{1}{1-\frac{2}{3}n\pi s^3},$$

or, using our former system of notation on which v represented the external volume, and b_1 the volume of the molecules contained within v,

$$\frac{v}{v-4b_1};$$

whence here again (p. 375)

$$\frac{l_3}{l_1}=\frac{v-4b_1}{v}.$$

This formula cannot, however, be pushed to the extreme limit of condensation of matter. Obviously not, if $v<4b_1$; for we should then obtain a negative mean free path. But the formula cannot even be used as far as this. l_1 was our free path when the molecules were without extension. Now l_1 must always remain greater than s, otherwise central impacts become impossible, and our formula no longer holds. This in fact happens if $v<8b_1$. It would have harmonized better with our general method of treatment to have called our "central impact" "double central impact," in those cases in which there is a central impact both at the beginning and end of a free path. How the value of the factor of b_1 diminishes with change of volume has not yet been ascertained. That it will become less than 4 seems clear from the disappearance of the central impacts, and of those impacts which can be considered nearly central. These play an especially important part in contributing to the magnitude of the factor. It may, however, be also expected that the double gliding impacts will disappear; in which case the factor 4 will not diminish so rapidly as might otherwise be anticipated.

If for the future we write b for $4b_1$ it will up to a certain limit represent four times the volume of the molecules, but beyond this limit a smaller multiple. Our former equation

$$\Sigma\tfrac{1}{2}m\mathrm{V}^2=\tfrac{3}{2}(\mathrm{N}+\mathrm{N}_1)v, \quad . \quad . \quad . \quad . \quad . \quad (\alpha)$$

will become

$$\Sigma \tfrac{1}{2} m V^2 = \tfrac{3}{2} (N' + N_1') (v - b). \quad . \quad . \quad . \quad (\beta)$$

For by a former remark the pressure must be directly proportional to the number of impacts, or inversely proportional to the mean free path. The mean free path is $\frac{v}{v-b}$ times shorter than that used in obtaining equation (α). Thus the pressure $N' + N'_1$ must be $\frac{v}{v-b}$ times greater than $N + N_1$; or

$$\frac{N' + N'_1}{N + N_1} = \frac{v}{v - b},$$

and thence arises equation (β).

[*Addition by the German Translator.*—In order to find the corrected equation (β) which arises from taking account of the size of the molecules, the original method in Chap. II. may be retained, as H. A. Lorentz shows (Wied. *Ann.* xii. pp. 127 -136, 1881). The method depends on the use of Clausius' equation of the virial. This equation is quite general, and so must hold for molecules of sensible size; provided that in the virial are included the repulsive forces which the molecules mutually exert during an encounter. (See Maxwell, 'Nature,' vol. x. p. 477.) We give part of Lorentz's development, as follows:—

Let A denote the virial $-\frac{1}{2}\Sigma(Xx + Yy + Zz)$ for the repulsive forces exerted at any instant by those molecules which are encountering each other. Then two encountering molecules P and Q contribute to A a part in which only the differences of the coordinates of the centres of P and Q occur. So that this part of the virial is connected with the size of the molecules, and for very small molecules may be neglected. On the supposition that during encounter the molecules change shape only insensibly, the part of the virial arising from P and Q is $-\frac{1}{2}K\sigma$, where K is the mutual impulse. Hence

$$A = -\tfrac{1}{2}\Sigma K\sigma,$$

the summation extending to all the pairs of molecules which are in the act of encounter at the instant considered.

At the first glance it would seem as if a closer knowledge of how the encounters take place would be necessary for this summation; since K, the force between two encountering molecules, depends on such a knowledge. A simple consideration, however, shows that a result can be arrived at without this knowledge as follows.

Instead of finding A for a given instant, we may take its mean value for a time τ very great compared with the time of an encounter. Thus

$$A = -\frac{1}{2\tau}\int \Sigma(K\sigma)d\tau = -\frac{\sigma}{2\tau}\int \Sigma(K)d\tau.$$

Now it is easily seen that instead of this we may write

$$A = -\frac{\sigma}{2\tau}\Sigma[\int K d\tau], \quad . \quad . \quad . \quad . \quad (3)$$

where the integration is first performed for each encounter taking place during the time τ, and the summation $\Sigma[\int K d\tau]$ is made for all these encounters. Now $\int K d\tau$ is equal to the product of the mass m of a molecule and the relative velocity of approach in the common normal U_n, and this independently of how the encounter takes place. Consequently

$$A = -\frac{m\sigma}{2\tau}\Sigma(U_n).$$

Now in order to find $\Sigma(U_n)$ we must both divide the encounters into groups, according to the circumstances under which they occur, and know the number of encounters in the time τ for each group. Strictly speaking, the same correction ought to be made here as was applied above, that is the correction to the number of encounters arising from the size of the molecules. The matter is simplified, however, if the influence of the virial arising from the repulsive forces, or the size of the molecules, is small, and if a correction to the first order is sufficient. Then the uncorrected value of the number of encounters may be used in calculating the small repulsive virial. The correction would only give rise to terms of higher order in the virial. In what follows, accordingly, we take the number of encounters as it usually is taken in such calculations.

Let $f(u)du$ represent the number of molecules contained within a volume of gas v the velocity of which is between u and

$u+du$. First, consider those encounters in which the velocity of one molecule is between u and $u+du$, the velocity of the other molecule between u' and $u'+du'$, the angle between the directions of the two velocities between ϕ and $\phi+d\phi$, and finally the acute angle between the relative velocity U and the common normal, between χ and $\chi+d\chi$. The number of these encounters during time τ is

$$\frac{\pi\sigma^2\tau}{v}f(u)du f(u')du' \mathrm{U} \sin\phi d\phi \sin\chi d\chi. \quad . \quad . \quad (4)$$

In each of these we have $\mathrm{U}_n = \mathrm{U}\cos\chi$, and multiplying this by (4), we get for $\Sigma(\mathrm{U}_n)$ the expression

$$\frac{\pi\sigma^2\tau}{v}f(u)\,du f(u')du'\,(u^2+u'^2-2uu'\cos\phi)$$
$$\sin\phi d\phi \sin\chi \cos^2\chi d\chi, \quad . \quad . \quad (5)$$

since $\mathrm{U}^2 = u^2+u'^2-2uu'\cos\phi$.

For the total $\Sigma(\mathrm{U}_n)$, this is to be integrated with respect to χ, ϕ, u', and u, the limits being 0 and $\frac{\pi}{2}$ for χ, 0 and π for ϕ, 0 and ∞ for u and also for u'. It must be observed that here each encounter is reckoned twice, and thus half the result is to be taken.

Finally,

$$\mathrm{A} = -\frac{\pi m\sigma^3}{4v}\int_0^\infty\int_0^\infty\int_0^\pi\int_0^{\frac{\pi}{2}} f(u)\,du\,f(u')\,du'\,(u^2+u'^2-2uu'\cos\phi)$$
$$\sin\phi d\phi \sin\chi\cos^2\chi d\chi = -\frac{\pi m\sigma^3}{6v}\int_0^\infty\int_0^\infty (u^2+u'^2)f(u)f(u')du\,du'.$$

Now if N is the number of molecules in volume v, and $\overline{u}^2$ the mean of the square of the velocities, then

$$\int_0^\infty f(u)\,du = \int_0^\infty f(u')\,du' = \mathrm{N},$$
$$\int_0^\infty u^2 f(u)\,du = \int_0^\infty u'^2 f(u')\,du' = \mathrm{N}\overline{u}^2;$$

hence

$$\mathrm{A} = -\frac{\pi m\sigma^3}{3v}\mathrm{N}^2\overline{u}^2.$$

This is the virial of the molecular repulsion. Combining this with the virial of the external pressure, which is $\frac{3}{2}pv$, the general equation of the virial gives

$$\tfrac{3}{2}pv-\frac{\pi m\sigma^3}{3v}\mathrm{N}^2\bar{u}^2=\Sigma\tfrac{1}{2}mu^2=\tfrac{1}{2}m\mathrm{N}\bar{u}^2$$

or

$$pv=\tfrac{1}{3}m\mathrm{N}\bar{u}^2\left(1+\tfrac{2}{3}\frac{\pi\sigma^3\mathrm{N}}{v}\right).$$

Now $\frac{2}{3}\pi\sigma^3\mathrm{N}$ is four times the volume of the molecules, and is therefore equal to b. Consequently

$$pv=\tfrac{1}{3}m\mathrm{N}u^{-2}\left(1+\frac{b}{v}\right);$$

or putting

$$\frac{1}{1+\frac{b}{v}}=1-\frac{b}{v},$$

the whole calculation being only to the first order of small quantities, and $\frac{b}{v}$ being supposed of this order, we get

$$p(v-b)=\tfrac{1}{3}m\mathrm{N}\bar{u}^2=\mathrm{R}(1+\alpha t), \quad . \quad . \quad . \quad (6)$$

which agrees with the former result.]

CHAPTER VII.

Relations between the Molecular Pressure and the Volume.

IN equation (β) (p. 385) if N' denotes the external pressure, then by our former investigations N_1' is the force with which the unit surface of the boundary layer is attracted inwards. N_1' depends on the degree of condensation of the material considered, and now we shall endeavour to express it as a function of the volume.

With this view consider an infinitely thin column in the boundary layer, and imagine a part of space below this layer, within the body, containing every molecule that could attract the column. If in this space there were a molecule at rest, we should require to know the law of force to be able to estimate its attraction on the column. But if this molecule is in motion, and can occupy any part of the space indifferently, the above difficulty for the most part disappears; and we can take the attraction exerted by the molecule to be the mean of the attractions which it would exert in its different possible positions in the space. The same consideration applies to a second molecule which may be within the space at the same time as the first. In short, the attraction exerted by the matter in the space mentioned is proportional to the quantity of matter, or to the density. The same holds for the molecules within the column, so that the attraction is proportional to the square of the density, or inversely proportional to the square of the volume. Hence we see that we arrive at the same result by considering the molecules moving as by considering the matter continuous, as is done in integration. We see further that gases are not to be included in this investigation, there being no molecular action in them. The attraction exerted on the boundary layer is small when the volume is very great; even if we could suddenly reduce the molecules of a gas to rest, no molecule would (on our supposition) act on another, and yet from the result got by considering the molecules as moving (viz. that the molecular pressure is proportional to the square of the density) a mean value could be found for the force with which the boundary layer is attracted inwards. Hitherto we have neglected the molecular forces within the mass, nor have we taken account of the effect of the motion on these forces. We are now in a position to take account of this effect if we consider that during a given time as many positive as negative forces act on a molecule within the mass. But if as many positive as negative forces act on the molecules, then at any point within the mass the sum of the moments of these forces, in other words, their virial, will be zero. Hence our equation of motion becomes

$$\left(p+\frac{a}{v^2}\right)(v-b)=\Sigma\tfrac{1}{3}mV^2\,; \quad . \quad . \quad . \quad . \quad (\gamma)$$

where p is the external pressure, v the volume, b a multiple of the molecular volume, and a the specific attraction. Since $\Sigma\frac{1}{3}mV^2$ increases with what is usually called the temperature, we can write for it,

$$\Sigma\tfrac{1}{3}mV_0^2(1+\alpha t).$$

Here α is understood to mean the hundredth part of the increase of the kinetic energy of the progressive motion of the molecules of a body when it is heated from the freezing-point to the boiling-point of water, the kinetic energy of the body being taken as unity at the freezing-point of water. This may be considered to give our definition of temperature.

If we had considered the whole kinetic energy instead of the kinetic energy of the progressive motion alone, we should have found the same value for α, provided we had assumed that the ratio of the two quantities of energy was independent of the density for a given body. This seems likely to be true, but cannot yet be proved. If we use equation (γ) for all degrees of density, for bodies in the gaseous as well as in the liquid form, then from the meaning which we have given to α it appears that we thus make the supposition that the kinetic energy of the progressive motion is independent of the density; that, for instance, a molecule of water and a molecule of steam at 0° have the same velocity of progressive motion. Certainly this supposition is more probable than that the whole kinetic energy of each is the same.

Further on we shall show by examples the accuracy of our equation as applied to liquids, and so justify our definition of α.

Equation (γ) can now be written

$$\left(p+\frac{a}{v^2}\right)(v-b)=\mathrm{R}(1+\alpha t) \quad . \quad . \quad . \quad . \quad (\delta)$$

Chapter VIII.

Applications of the Isothermals.

(a) *The Pressure-Coefficient.*

Before we investigate whether equation (δ) is confirmed by observation we will investigate how the constants a and b depend on t. That a does not depend on t is clear from its meaning; at least, we shall scarcely attribute to the attraction the peculiar property of being a function of the temperature. But for b we cannot be so certain. Are the molecules of a body larger at higher temperatures? Or, rather, does the temperature influence the limiting distance of approach of the molecules during encounter? On account of the uncertainty of the answer to this question I have neglected the effect of a possible expansion of the molecules; and further researches must show how far this is justifiable.

Since the equation is less simple when v is regarded as a variable, we naturally determine the changes in the expression on the left-hand side when v remains constant. We imagine the body first at 0° and afterwards at $t°$, and investigate the increase of pressure.

Thus

$$\left(p_t+\frac{a}{v^2}\right)(v-b)=\mathrm{R}\,(1+at)$$

and

$$\left(p_0+\frac{a}{v^2}\right)(v-b)=\mathrm{R}.$$

Subtracting, we get

$$(p_t-p_0)\,(v-b)=\mathrm{R}\,\alpha t,$$

or

$$\frac{p_t-p_0}{p_0}=\left(1+\frac{a}{p_0v^2}\right)\alpha\, t. \quad . \quad . \quad . \quad . \quad .\text{(A)}$$

Generally

$$\frac{p_{t_2}-p_{t_1}}{p_0}=\left\{1+\frac{a}{p_0v^2}\right\}\alpha\,(t_2-t_1). \ . \ . \quad . \quad . \quad \text{(B)}$$

Let us call $\dfrac{p_t-p_0}{p_0t}$ the pressure-coefficient and denote it by α_p,

then
$$\alpha_p=\left(1+\frac{a}{p_0v^2}\right)\alpha.$$

From this equation two important consequences follow :—

First, on the right-hand side, if v is constant and the original pressure or the original density constant also, no quantity occurs depending on t. Hence, "for the same density the pressure-coefficient is independent of the temperature." In this there is no mention of a mean pressure-coefficient between 0 and t degrees, and consequently for constant volume the pressure of the body must afford a simple measure of the temperature.

Whether experience confirms this consequence of our equation may be determined by an investigation of Regnault (*Mém. de l'Acad.* xxi. p. 180 *et seq.*) on the comparison of different gas-thermometers.

Regnault finds that thermometers filled with different gases, including carbonic acid, gave in general identical readings up to over 300° C. The one filled with sulphurous acid alone, though agreeing with the air-thermometer both at 0° and near 100°, failed to keep pace with this latter at higher temperatures. Regnault infers from this that gas-thermometers may be filled with different gases and will yet give concordant readings; sulphurous acid, however, must be excepted, since its pressure-coefficient diminishes with the temperature. Thus we have a decided contradiction to a most reasonable expectation deduced from our equation.

The exactly opposite view has often been taken as the more probable one. Definite statements are seldom made; but the old saying that "Rise of temperature makes a gas approach the ideal state" merely indicates that the pressure-coefficient is expected to become less and less at higher temperatures, and to approach a limit ascribed to ideal gases. I must admit that the behaviour of sulphurous acid caused me some difficulty at first. If I am not in a position to give a sufficient reason for this anomaly, then my proposition that rise of temperature does not make a gas or vapour approach the so-called ideal state more nearly is not valid; and the equation I have given is untenable. I therefore considered every circumstance which could cause a falling off of pressure at high temperatures, but without any satisfactory result. The matter, however, may be viewed otherwise, and it may be asked:—Is there any reason why at low temperatures the pressure should increase more rapidly than the rise of temperature demands? Now, a reason can be assigned for this phenomenon if it occurs in ordinary experiments. At low temperatures a layer of gas is condensed on the walls of the containing vessel, and as the temperature rises this layer either suddenly or slowly tends to evaporate. If this happens it is clear that at the moment when the evaporation takes place there will apparently be a too rapid rise of the pressure-coefficient. That this hitherto unexplained phenomenon sometimes takes place was observed by Pouillet in his experiments on platinum surfaces, and lately it has been established by Herwig in his investigations on ether, alcohol, &c. in glass vessels*.

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* [It seems almost certain that vaporization is the principal cause of the variations mentioned above. Chappuis (Wied. *Ann.* viii. p. 1, and 671,

It is to be expected that when the gas condensed on the walls of the containing vessel has become vaporized at a certain temperature, and the quantity of gas in the constant space thereafter remains unchanged, the pressure-coefficient will remain constant with increase of temperature. Now Regnault certainly implies that it constantly diminishes, being (according to him) 0·0038251 between 0° and 98°·12, and only 0·0037893 between 0° and 310°·31. He thus suggests the expectation that since the mean coefficient diminishes so much, the true coefficient will diminish still more; and moreover that there will be a rate of change of this coefficient per degree of temperature which may depend on the temperature. This expectation, however, is not logically justified. If we endeavour to obtain the true and not the mean coefficient from Regnault's observations, we always find that the true is constant and less than the mean from 98°·12 up to any temperature to which the thermometers are raised. From 98°·12 onwards the constancy of α_p is so complete that there is more agreement between the readings of these two thermometers (air and sulphurous-acid) than between any others examined by Regnault.

A simple calculation will show this. Let t be the temperature up to which the thermometers keep together, and let ϵ_p be the mean pressure-coefficient of sulphurous acid between 0° and $t°$, then

$$\frac{P_t - P}{P_0} = \epsilon_p t. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If P′ is the pressure shown by the sulphurous-acid thermometer, then the temperature indicated by it is given by

$$\frac{P' - P_0}{P_0 \epsilon_p} = t'. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

But a_p is the true pressure-coefficient for all temperatures above t; and therefore it is clear that t' cannot be the true

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1879) finds that from 1·6753 square metres of glass surface 1·03 c. cm. of sulphurous acid are vaporized between 0° and 180°; Bottomley, Chem. News, 51-85, 1885; Callendar, Phil. Trans. 1887; Kayser, Wied. *Ann.* 1881.—*Note by the German Translator.*]

temperature. Let t_1 denote the true temperature obtained from our fundamental formula

$$\frac{P'-P_t}{P_0}=\alpha_p(t_1-t).$$

Subtracting equation (1) from (2) we get

$$\frac{P'-P_t}{P_0}=\epsilon_p(t'-t),$$

or

$$\epsilon_p(t'-t)=\alpha_p(t_1-t),$$

or

$$\frac{\alpha_p}{\epsilon_p}=\frac{t'-t}{t_1-t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

In this equation t' and t_1 denote the two temperatures simultaneously shown by the sulphurous-acid thermometer and the air-thermometer. Conversely (3) enables us to find t_1 from t' when α_p is known. Accordingly, if we take $\alpha_p=0{\cdot}0037725$, we find the temperatures for the sulphurous-acid thermometer from equation (3). In the following table these are given under *a*, the temperatures for the air-thermometer under *b*, and the differences under *c*.

a.	*b.*	*c.*	*a.*	*b.*	*c.*
98·12	98·12	0	257·10	257·17	−0·07
102·44	102·45	−0·01	299·94	299·90	+0·04
185·39	185·42	−0·03	310·31	310·31	0

The differences are less than anywhere else in Regnault's comparisons, exactly as if he had made more accurate observations when there was a surprising difference between the two thermometers than he did when the agreement was better. A second set of Regnault's observations gives a similar result. The observations consisted of a series of comparisons at low pressures between the sulphurous-acid and the normal thermometer. By our equation

$$\alpha_p=\left\{1+\frac{a}{p_0v^2}\right\}\alpha$$

it appears (as we shall see immediately) that α_p is smaller when the density is smaller.

Regnault found that the thermometers agreed up to 97°·56 when he took $\epsilon_p=0\cdot003794$. Taking $\alpha_p=0\cdot0037438$ and proceeding as above with this set of his observations, we get the following table, arranged as before :—

a.	*b.*	*c.*	*a.*	*b.*	*c.*
97·56	97·56	0	229·38	229·38	0
137·30	137·24	0·06	260·89	260·84	0·05
195·50	195·42	0·08	320·67	320·68	−0·01
228·31	228·16	0·15			

These differences are also less than those obtained in experiments on other thermometers where Regnault himself was satisfied with the agreement. For both the thermometers the initial point of the range of temperature over which α_p is measured is the same, thus agreeing with the present theory; also for both the thermometers the difference of ϵ_p and α_p is the same. In the first set of observations this difference is 0·000052, and in the second 0·0000502. The meaning of the equality of these differences appears as follows :—

Let P_1 be the pressure in the apparatus when α_p commences, that is at temperature t; and let P_t be the pressure at t when all the condensed gas has been dislodged from the walls of the containing vessel. Then

$$\frac{P_1-P_0}{P_0}=\epsilon_p t$$

and

$$\frac{P_t-P_0}{P_0}=\alpha_p t,$$

therefore

$$\frac{P_1-P_t}{P_0}=(\epsilon_p-\alpha_p)\,t.$$

The right-hand side of this equation is the same for both thermometers, therefore the left-hand side is the same for both. The meaning of the identity of the left-hand sides of the equation for both thermometers is that the quantity of gas dislodged from the sides of the containing vessel between 0 and t° is proportional to the quantity of gas originally present.

At one time I went into this subject in detail, so as to draw attention to the deviations still to be explained, even supposing our theory to be accepted, and thus to give warning of the precautions necessary in the determination of the pressure-coefficient. For example, we should in this case have found too great a pressure-coefficient for sulphurous acid if we had been satisfied with investigating it up to 100°. I also expected to see a striking confirmation of my anticipations in this phenomenon, which at first sight apparently contradicted my theory. At all events, it was due to theory that I was led to discover the constancy of α_p. If this fact had not been clearly indicated by theory, I should never have sought to discover its experimental verification.

A second important consequence which can be deduced from the equation

$$\alpha_p = \left\{1 + \frac{a}{p_0 v^2}\right\} \alpha$$

is the dependence of α_p on the density. For all substances $\alpha_p > \alpha$, and this difference becomes greater as the value of a increases, and the difference also becomes greater the greater the value of p_0 or of the density.

We shall see below that a is insensibly small for hydrogen; so that for this gas $\alpha_p = \alpha$; and thus we have a means of determining α. The researches of Regnault and of Magnus on the pressure-coefficient of hydrogen do not completely agree; but 0·00366 cannot differ sensibly from the value of α. We can show the correctness of the supposition that $a=0$ for hydrogen, by a set of Regnault's observations made to determine α_p for different densities. If $a=0$ then α_p must be the same for every density. Regnault found that there was no observable change in α_p when the original pressure was from 1 to 4 atmospheres, and this was not the case in any other gas investigated (Regnault, *Mém. de l'Acad.* xxi. p. 116, 1847).

A similar investigation by Regnault for carbonic acid gas shows clearly that in this case a has a sensible value. If a rigorous determination of a is required the equation

$$\alpha_p = \left\{1 + \frac{a}{p_0 v^2}\right\}\alpha$$

must be considered simultaneously with

$$\left(p_0 + \frac{a}{v^2}\right)(v - b) = \mathrm{R}\,(1 + \alpha t).$$

Then b would also have to be known. However, even the experiments of Regnault do not permit of a rigorous determination, and we can hope for no agreement so long as the experiments at our disposal present us with such discrepancies. For instance, in the case of carbonic acid gas, Regnault obtains two values of α_p at the same pressure—that of one atmosphere—in two different series of experiments. In one (*Mém. de l'Acad.* xxi. p. 112, 1847) he gets $\alpha_p = \cdot 0036856$; and in another (*Mém. de l'Acad.* xxi. p. 182, 1847), $\alpha_p = \cdot 003695$.

Since we can only assign an approximate value to this quantity, it is sufficiently accurate to put

$$\alpha_p = \{1 + a p_0\}\alpha,$$

when the condensation is not too great. This equation expresses the proportionality of the increase of the pressure-coefficient to the density. A more accurate value of a is given by the equation

$$\alpha_p = \left\{1 + \frac{a p_0}{p_0^{\,2} v_0^{\,2}}\right\}\alpha.$$

Thus, for carbonic acid the product $p_0 v_0$ decreases at high pressures, and the amount of this decrease is known from Regnault's researches on the limits within which Boyle's Law is applicable to this gas.

Let the unit of pressure be that due to 1 metre of mercury, and the unit of volume the volume of 1 kilogram of gas at 0° and under a pressure of 1 metre of mercury; then we get the following values for a by means of the value of α_p which Regnault gives for the pressures in the first column.

At 0·758, . . .	$a = 0{\cdot}0099$	$a = 0{\cdot}0125$
„ 0·901, . . .	$a = 0{\cdot}0103$	$a = 0{\cdot}0125$
„ 1·742, . . .	$a = 0{\cdot}013$	
„ 3·589, . . .	$a = 0{\cdot}015$	

I can assign no reason for the great differences shown here, and Regnault himself is satisfied with simply stating the result, a course of procedure unusual in his accounts of his experiments. From the investigations given below it will appear that by putting $a=0{\cdot}0115$, the whole behaviour of carbonic acid is rendered clear, the same units being understood. This number means that in carbonic acid at 0° and 1 metre pressure the inward attraction on the boundary layer is equal to a pressure of 0·0115 metres of mercury.

Again, the two former values of α_p for sulphurous acid referring to different densities, viz. 0·0037725 at 0·7515 m. pressure and 0·0037434 at 0·5887 m. pressure, enable us to show the correctness of the equation for α_p. From the former the approximate value of a is 0·040; and from the latter $a=0{\cdot}039$. Here we have the values for sulphurous acid freed from possible errors, and may therefore expect for the values of a a tolerably good agreement.

The investigation of a for air suggests the following remarks.

We find the values of a by help of the pressure-coefficient given by Regnault (*Mém. de l'Acad.* xxi. p. 110, 1847) for pressures above one atmosphere :—

Pressure.	Pressure-coefficient.	a.
3·655	0·0037091	0·0037
2·144	0·0036894	0·0038
1·692	0·003680	0·0033
1·678	0·003676	0·0025
0·76	0·003665	0·0017

Only the first three are satisfactory, the last two differ widely. However, it is only necessary to take the fourth pressure-coefficient $=0{\cdot}0036786$ in order to get $a=0{\cdot}003300$ again. At the pressure 1·678 m. Regnault quotes only two observations, one of which gives $\alpha_p=0{\cdot}0036734$, while the other gives the value which I have chosen to use here. It will be noticed that Regnault's estimates differ considerably in the sixth decimal place, as is often the case at low pressures. So that if by a slight change in this decimal place concordant values of a can be found, those estimates will not weigh against our formula. Later we shall find $a=0{\cdot}0037$.

Regnault himself admits the untrustworthiness of his values for the pressure-coefficients below one atmosphere (some of them going so low as 0·0036482), yet he takes 0·003666 as the limiting value for α_p when the density continually diminishes. The number 0·0036639 is contained among others in the set of experimental results from which Regnault takes the value 0·0036482.

(b) *The Compressibility of Gases.*

Hitherto we have considered v constant. Now we shall take t as constant, and examine whether the relation between v and p given by

$$\left(p+\frac{a}{v^2}\right)(v-b)=\mathrm{R}\ (1+\alpha t)$$

is confirmed by experiment. With this view we use the results found by Regnault in his researches on Boyle's law.

First, for atmospheric air. Regnault arranged his experiments as follows :—He endeavoured to determine the quotient $\frac{p_1 v_1}{p_0 v_0}$ for different initial pressures, the volume always being reduced to about one half. A definite law can scarcely be formulated from the results, and therefore Regnault contented himself with an empirical formula, which, however, does not completely represent the observations, especially at high pressures. This formula is

$$pv=1-\mathrm{A}\left(\frac{1-v}{v}\right)+\mathrm{B}\left(\frac{1-v}{v}\right)^2$$

or

$$pv=(1+\mathrm{A}+\mathrm{B})-\frac{\mathrm{A}+2\mathrm{B}}{v}+\frac{\mathrm{B}}{v^2}.$$

We may write our equation

$$pv=(1+a)\,(1-b)\,(1+\alpha t)-\frac{a}{v}+\frac{ab}{v^2}+bp,$$

taking with Regnault for unit of pressure the pressure due to 1 metre of mercury, and for unit of volume the volume of the quantity of gas considered, at 0°, under this pressure.

At low pressures, where p may be replaced by $\frac{1}{v}$ without much error, the empirical formula of Regnault agrees with our equation. Then A+2B will give us an approximate value for $a-b$. This is about 0·0011. Hence by means of the value which we took for a, 0·0037, we get $b=0·0026$. We must have B very nearly equal to the product ab if Regnault's empirical formula completely corresponds to observation. Now B is 0·0000194, while our product ab is only about half of this. Hence our equation gives a higher compressibility than does Regnault's; and we find the compressibility of air to be really greater than that given by his formula for the highest pressures observed by him.

We previously decided that a must be very small for hydrogen, from the fact that α_p is independent of the density. Regnault's investigation of the compressibility at constant temperature confirms this completely. For hydrogen our equation takes the simpler form

$$p(v-b)=(1-b)(1+\alpha t),$$

or

$$pv=(1-b)(1+\alpha t)+bp,$$

and

$$\frac{pv}{p_1v_1}=\frac{(1-b)(1+\alpha t)+bp}{(1-b)(1+\alpha t)+bp_1}.$$

If p_1 is the greater pressure, the right-hand side is a proper fraction, and therefore $p_1v_1>pv$.

Regnault gives (*Mém. de l'Acad.* xxi. p. 344, 1847) for $p=2·211$ and $p_1=4·431$, the temperature being 4·4 degrees,

$$\frac{pv}{p_1v_1}=0·998584\,;$$

hence we get $b=0·00065$. For $p_2=10·715$ m. he gives

$$\frac{pv}{p_2v_2}=0·994676\,;$$

hence we again get $b=0·00065$. It is of little use to give the value of b for all Regnault's experiments on hydrogen, since his observations are very often not concordant. Thus, by combining observations Nos. 24 and 25 at pressures 9·176 and 18·490, we find $\frac{pv}{p_1v_1}=0·992933$; and from Nos. 31 and 32 at about the same pressures we get 0·993618.

The first gives $b=0{\cdot}00077$; the second gives $b=0{\cdot}00065$. The extreme values of b are 0·0005 and 0·0008, and the mean value of a great number of Regnault's observations gives 0·00069.

This result expresses the fact that the molecules of a volume of hydrogen at 0° and under a pressure of 1 metre of mercury occupy only $\frac{1}{4}\times 0{\cdot}00065$ of the whole volume. For air we found $b=0{\cdot}0026$. Thus the molecules of air are about four times as large as the molecules of hydrogen; and we might possibly have expected to find an even lower value for the latter. For, considering that the oxygen molecule is 16 times, and the nitrogen molecule 14 times heavier than the hydrogen molecule, one might be inclined to anticipate that this would be the ratio of the volumes. But it must be remembered that the volume here taken is not necessarily the same as the sum of the volumes of the atoms composing the molecule. The molecule is an aggregate consisting of matter and empty space. If we wished to draw a general conclusion from these two examples, we should say that the molecular volume is proportional to the square root of the specific gravity of the gas. The result found for carbonic acid agrees very well with this supposition *.

The result found for hydrogen shows us how arbitrary in general is the prevailing conception of ideal gases supposed to be defined as those which follow Boyle's and Gay Lussac's laws. We see from what has been said that the most perfect gas, in which there is no attraction to speak of, must necessarily deviate from these laws. The ordinary conception of ideal gases, if realized, would give us bodies deprived of the single essential property of matter-extension in space. Indeed, if we had a substance which followed Boyle's law within fixed limits of density, the reason would be that a and b were for that substance of nearly equal value. Then so-called ideal gases would be those in which the constant of the molecular volume is equal to the specific attraction. It cannot be denied that the customary definition

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* [The numbers found later for other substances do not, however, bear out the rule; so there is perhaps more probability in the supposition that the molecular volume is closely connected with the sum of the atomic volumes.—*Note by the German Translator.*]

of a perfect gas is quite arbitrary; and therefore Regnault is right in saying ironically that hydrogen would have to be a "*gaz plus que parfait*" if Boyle's law were a real criterion of perfection in gases.

A similar investigation for carbonic acid gives for the difference between a and b the value 0·0085. The probable value of a is 0·0115, and therefore $b=0\cdot003$. Thus, for carbonic acid the equation becomes

$$\left(p+\frac{0\cdot0115}{v^2}\right)(v-0\cdot003)=1\cdot00846\,(1+\alpha t).$$

This equation gives the compressibility much better than does Regnault's empirical formula. From the many series of experiments by which we can test the equation, I choose the 9th set, at the same time as an example of the use of the method and as most conveniently verifying it.

In this set the original pressure was about 8·4 m. In some experiments the volume was reduced to one half; in others to the $\frac{1}{2\cdot87}$th part. The original pressure, 8·4 m., corresponds according to our equation to the volume $\frac{1}{9}$; or, more accurately, a volume $\frac{1}{9}$ corresponds to a pressure 8·509 m. Similarly, as in the following table, we get

Volume.	Calculated Pressure.	VP.
(1) $\frac{1}{9}$	8·509	$\frac{8\cdot509}{9}$
(2) $\frac{1}{18}$	15·694	$\frac{15\cdot694}{9\times2}$
(3) $\frac{1}{9\times2\cdot87}$	20·905	$\frac{20\cdot905}{9\times2\cdot87}$

Calculated Ratio.		Observed Ratio.
$\frac{(1)}{(2)}$	1·0844	1·0845
$\frac{(1)}{(3)}$	1·1673	1·1694 1·1666

With $b=0\cdot003$ Regnault's different sets of experiments give the following approximate values for $a\,.\,10^4$:—

127, 114, 115, 107, 120, 113, 116, 111, 116.

Excluding the first, which corresponded to the smallest pressure, and therefore is least trustworthy, we find for a the value 0·0114.

(c) *The Coefficient of Expansion.*

The two variations of condition to which we have hitherto subjected a gas, served only for the computation of a and b. In the remaining admissible variations we have a means of testing the accuracy of the values determined; the most simple test is by heating at constant pressure, and this is the one most frequently investigated.

In this case let us call $\frac{v_t - v_0}{v_0 t} = \alpha_v$ the coefficient of expansion. The determination of v_t is given by

$$\left(p + \frac{a}{v_t^2}\right)(v_t - b) = (1+a)(1-b)(1+\alpha t); \quad . \quad . \quad (\mathrm{E})$$

and for v_0 we have

$$\left(p + \frac{a}{v_0^2}\right)(v_0 - b) = (1+a)(1-b). \quad . \quad . \quad . \quad . \quad (\mathrm{E}_1)$$

By eliminating p we get v as a function of t.

The general formula is not simple. For hydrogen we get

$$\alpha_v = \left(1 - \frac{b}{v_0}\right)\alpha.$$

Here α_v is independent of t, but depends on the density. Thus in this case the expansion at constant pressure will afford a simple measure of the temperature, which is not the case in other gases; and further, for hydrogen $\alpha_v < \alpha_p$. But the difference between α_v and α_p is too small to be closely determined by experiment, if the pressure is not very great.

We shall also examine whether the constants previously obtained agree with the values for α_v given by Regnault (*Mém. de l'Acad.* xxvi. p. 571, 1849), for air at various densities. We shall assume that Regnault's method of determining the coefficient of expansion for pressures from 3·8473 to 14·4145 m. is known. In equation (E), if p and v_t are known, we get a relation between a and b from each of his observations. The quantity v_t is found by multiplying v_0 given in equation (E_1) by $(1 + \alpha_v t)$ as determined in the observations.

For the sake of simplicity I have used the values calculated by Regnault from his formula, and the directly observed values of v_0. Taking $b=0{\cdot}0026$ m. as before, and the values of α_v as given in the following table, we get the values of a :—

$\alpha_v . 10^7$.	$a . 10^5$.	Pressure.
37242	367	3·857
37668	358	6·554
37825	375	10·429
37826	390	10·578
38012	385	11·640
37974	414	12·972
38422	352	14·414

Omitting the value $a={\cdot}00414$, which results from an obviously erroneous value of α_v, we get $a=0{\cdot}0037$.

I shall treat other values of Regnault's (*Mém. de l'Acad.* xxi. p. 115, 1847) somewhat differently, so as to show what form the equations take when arranged for testing the values of a and b at low pressures. Let us write $v_t=vx$ [where v is put instead of v_0 and x denotes $1+\alpha_v t$], then we easily get from equations (E) and (E_1) the following :—

$$\frac{x-1}{t}\left\{1-\frac{a}{(1+a)(1-b)}\frac{1}{v}\frac{x+1}{x}+\frac{b}{v-b}+\frac{ab}{(1+a)(1-b)v^2}\frac{x+1}{x}\right\}=\alpha,$$

or

$$\frac{a}{(1+a)(1-b)v}\frac{x+1}{x}-\frac{b}{v-b}-\frac{ab}{(1+a)(1-b)v^2}\frac{x+1}{x^2}=\frac{x-(1+\alpha t)}{x-1}. \qquad (E_2)$$

According to Regnault we have :—

Pressure.	α_v.
0·760	0·0036706
2·525	0·0036944
2·620	0·0036964

By means of these values we arrive at the following approximate equations in which the product ab is neglected, $\frac{x+1}{x}$ is put$=1{\cdot}73$, and $v=\frac{1}{p}$; all of these simplifications introducing only very slight changes.

$$\frac{a}{(1+a)\,(1-b)}\,2{\cdot}62\times 1{\cdot}73-\frac{b}{(1+a)(1-b)}\,2{\cdot}62\;=0{\cdot}0098,$$

$$\frac{a}{(1+a)\,(1-b)}\,2{\cdot}525\times 1{\cdot}73-\frac{b}{(1+a)(1-b)}\,2{\cdot}525=0{\cdot}0093,$$

$$\frac{a}{1+a)\,(1-b)}\,0{\cdot}76\times 1{\cdot}73-\frac{b}{(1+a)\,(1-b)}\,0{\cdot}76=0{\cdot}0029\;;$$

or approximately,

$$1{\cdot}73a-b=0{\cdot}00374,$$
$$1{\cdot}73a-b=0{\cdot}00369,$$
$$1{\cdot}73a-b=0{\cdot}00381;$$

and since, from the investigations on Boyle's law, $a-b=0{\cdot}0011$, it follows that

$$a=0{\cdot}0036,$$
$$a=0{\cdot}00355,$$
$$a=0{\cdot}0037.$$

From equation (E_2) it also appears that the gases for which $1{\cdot}73\,a=b$ have their coefficient of expansion $=\alpha$ between 0° and 100°, the pressure not being high. If $1{\cdot}73\,a<b$, then $\alpha_v<\alpha$. This is a further proof of the arbitrariness of the prevailing view as to ideal gases, viz. that they are to be recognized by the equality of α_v and α. We often meet with the assertion that α_v is always greater than α_p, perhaps because it is sometimes observed to be so. The following equation, however, shows that the converse is quite possible, and that for air there is almost complete equality between these two quantities.

By suitably combining equations (E) and (E_2), and remembering the values of α_v and α_p, we get generally

$$v_0(\alpha_v-\alpha_p)=\frac{a\,\alpha_v}{p_0\,v_0(1+\alpha_v\,t)}\left\{1-\frac{b}{v_0}\cdot\frac{2+\alpha_v\,t}{1+\alpha_v\,t}\right\}-b\,\alpha_p.$$

This becomes approximately, if the pressure is not too high,

$$v_0\,(\alpha_v-\alpha_p)=a\frac{\alpha_v}{1+\alpha_v\,t}-b\,\alpha_p.$$

When $\frac{a}{1+\alpha\,t}<b$, then $\alpha_v<\alpha_p$. For air at 100°, $\frac{a}{1+\alpha t}$ is nearly equal to b; for $\frac{0\cdot0037}{1\cdot366}$ is nearly 0·0027, which is a little greater than b. Hence α_v and α_p are nearly equal. The following numbers show this :—

Pressure.	$\alpha_p \,.\, 10^6$.	Pressure.	$\alpha_v \,.\, 10^6$.
0·76	3665	0·76	3670
1·678	3676	……	……
1·692	3680	……	……
2·144	3689	……	……
……	……	2·525	3694
……	……	2·62	3696
3·655	3709	……	……
……	……	3·857	3724

We may conclude that at 100° and under a given pressure $\alpha_p = \alpha_v$. But since we know that α_p is independent of the temperature, it appears from the above equation for $\alpha_v - \alpha_p$ that α_v must be a function diminishing with the temperature. Thus, we are not justified in following Regnault when he regards any possibly practicable constant-pressure thermometer as necessarily giving concordant results whatever may be the gas with which it is filled.

I have made a similar investigation for carbonic acid, using a set of Regnault's observations of α_v at pressures differing widely from one another. From these it appears that the most probable values are $a = 0\cdot0115$ and $b = 0\cdot003$.

More recently, Andrews (Pogg. *Ann.* Ergsbd. v. p. 61, 1871) has published investigations on carbonic acid at very various pressures, temperatures, and volumes; and these are more suited to test our equation than any others. We may remark here that for carbonic acid the difference between α_v and α_p is considerable, and increases with the pressure, as the inequality $\frac{a}{1+\alpha t} > b$ would lead us to expect.

(d) *Experiments of Andrews.*

In Andrews's experiments the volume and temperature are directly determined, while the pressure is measured by means of the compression, or better by means of the volume of an enclosed quantity of air. In order to determine the pressure by this method it is necessary to make use of the equation given above, connecting the pressure and volume. The constants, however, ought to be determined more accurately than we have hitherto succeeded in doing. Therefore the following sets of calculated values are not to be considered exact. I have not determined the pressure of the air in each experiment by my equation, but have thought it sufficient to use a correction which gives about the mean of the values arising from my equation and from Regnault's empirical formula. This can only very slightly affect the general result.

Andrews's investigations extend to pressures up to 110 atmospheres, and in consequence densities were observed 500 times greater than the density at one atmosphere. There was some doubt about using the constants for carbonic acid determined from Regnault's investigations, in which the pressure was 27 atmospheres at most. The result was, however, so satisfactory that it seemed better to work with these numbers than to begin by seeking for the most probable values of a and b from Andrews's experiments themselves. Andrews's units of pressure and volume are not the same as Regnault's, and have the advantage of being more usual; thus, his unit of volume is the actual volume of the carbonic acid at 0° C. and under a pressure of one atmosphere, and his unit of pressure is one atmosphere. In consequence of this, the constants have to be altered as follows:—At a pressure of one atmosphere the volume is about $\frac{1}{0{\cdot}76}$ of the volume at 1 metre pressure. Since the molecular pressure, which is added to the external pressure, is proportional to the square of the density, it now becomes $0{\cdot}0115 \times 0{\cdot}76^2$ metres or $0{\cdot}0115 \times 0{\cdot}76$ atmospheres. But b will also be altered: from the definition of b the space occupied by the molecules of a given weight of carbonic acid is

$\frac{0·003}{4}$ of the apparent volume of the gas. Expressing this apparent volume in units $\frac{1}{0·76}$ times as great as the old units the new value of b becomes $0·003 \times 0·76$. Thus our equation for carbonic acid becomes

$$\left(p+\frac{0·00874}{v^2}\right)(v-0·0023)=1·00646\,(1+\alpha t).$$

From Andrews's data v can be determined quite accurately. The real volume is always stated by Andrews as a fraction of the volume which the carbonic acid would take at the same temperature and at unit pressure. For a I have taken the value 0·00874 as correct, and from it I have found $\frac{a}{v^2}$. This quantity expresses in atmospheres the amount added by attraction to the pressure caused by the reaction to the molecular motion. Knowing also the external pressure, as determined by the volume of air in the manometer, we get the value of $v-b$; and, v being known, we calculate b. At temperatures below 30°·9 the carbonic acid becomes easily liquefied; and the volume of the non-homogeneous mixture of gas and liquid ceases to have any definite significance.

The Table on p. 409, which needs no further explanation, gives the values of b.

If we consider that an error in a becomes much more sensible in $\frac{a}{v^2}$, and similarly affects b, and, further, that the experiments of Andrews do not altogether represent the actual process, since a small quantity of air was present, we may regard the concordance as indeed striking. At the highest pressures the value of $\frac{a}{v^2}$ amounts to far above 1000 atmospheres.

For volumes above 0·0046 we may regard the values of b as constant, at least for the same temperature. At higher temperatures this constant value of b is somewhat greater; but the value of a being only approximate, as well as the other slight inaccuracies attaching both to the experimental

t, 13°·1.	t, 21°·5.	t, 32°·5.	t, 35°·5.
v=0·013764	v=0·016044	v=0·013038	v=0·01367
b=0·00242	b=0·00241	b=0·00251	b=0·0025
v=0·013036	Mixture of gas	v=0·0079777	v=0·012716
b=0·00234	and liquid.	b=0·00254	b=0·0025
v=0·012933	"	v=0·0071736	v=0·01173
b=0·00239	"	b=0·00252	b=0·0027
Mixture of gas	"	v=0·006999	v=0·0106
and liquid.		b=0·002513	b=0·0025
"	"	v=0·006277	v=0·00955
"	"	b=0·00248	b=0·00244
"	"	v=0·0038415	v=0·00837
"	"	b=0·002157	b=0·00254
"	Liquid.	v=0·003188	v=0·007016
"	v=0·002935	b=0·00199	b=0·0025
"	b=0·001924	v=0·00289	v=0·00496
"	v=0·0024526	b=0·00190	b=0·00234
"	b=0·001734		v=0·00321
"	v=0·0024288		b=0·0020
Liquid.	b=0·001719		v=0·003026
v=0·0022647			b=0·00195
b=0·001663			v=0·00275
v=0·0022234			b=0·00184
b=0·001643			v=0·002629
v=0·0021822			b=0·001798
b=0·001627			
v=0·0020937			
b=0·001585			
v=0·0020527			
b=0·001565			

and the theoretical investigation, make the conclusion that b increases with the temperature seem very hazardous. We know *à priori* that the value of b must diminish for volumes less than $0·0046=2\,b$. It is a most important result that at widely differing temperatures a smaller value of b always corresponds to a smaller volume, so that any possible influence of the temperature disappears so far as b is concerned. Consequently the variability of b, the law of which we do not yet know, no longer appears arbitrary and meaningless. Setting aside the consideration of the temperature, a definite value of b corresponds to a definite value of v; and, as appears from our previous researches, this quantity will have a value entirely dependent on the possible modes of molecular motion.

As an example I will show the utility of the equation with the constants already chosen, by calculating p directly.

Andrews observed that at 13°·2 the volume of the carbonic acid was reduced to $\frac{1}{76 \cdot 16}$, under a pressure sufficient to reduce a volume of air at 10°·4 to $\frac{1}{47 \cdot 3}$ of its original volume. The calculation of p from the data for air and carbonic acid is as follows; the two values of p ought evidently to be the same:—

For Carbonic Acid.

$$v=\frac{1+13 \cdot 2 \times 0 \cdot 00368}{76 \cdot 16}=0 \cdot 013767\,;$$

$$v-b=0 \cdot 01148\,;$$

$$(1+a)(1-b)(1+\alpha t)=1 \cdot 0552\,;$$

$$p+\frac{a}{v^2}=\frac{1 \cdot 0552}{0 \cdot 01148}=91 \cdot 9 \text{ atm.}\,;$$

$$\frac{a}{v^2}=46 \text{ atm.}\,;$$

$$p=45 \cdot 9 \text{ atm.}$$

For Air.

$$v=0 \cdot 0219\,;$$

$$v-b=0 \cdot 019926\,;$$

$$(1+a)(1-b)(1+\alpha t)=1 \cdot 040\,;$$

$$p+\frac{a}{v^2}=52 \cdot 2 \text{ atm.}\,;$$

$$\frac{a}{v^2}=6 \text{ atm.}\,;$$

$$p=46 \cdot 2 \text{ atm.}$$

This concordance seems sufficient to prove the value of the two equations.

It may perhaps be granted that the theory holds for gases, though some hesitation may be experienced in extending it to liquids, because by doing so we implicitly ignore the difference between the two states. In our treatment of the surface phenomena we regarded the two conditions in question as the two extremes; but the experiments of Andrews and the values of b calculated from them show that doubts as to the legitimacy of the extended method may be safely abandoned. With a volume between 0·003 and 0·0025, at 21°·5 the substance exists entirely in the liquid state, and at 35°·5 entirely in the gaseous state. Taking a and b to have the same value for each state, our equation may be applied to both states.

[*Addition by the German Translator.*—The foregoing considerations show how difficult it becomes to arrange investigations on the compressibility of gases within wide limits of pressure and temperature with such accuracy that the observations may be profitably compared with the theoretical equation. Even the values given by such a scrupulous and skilful experimenter as Regnault, whose investigations are classical, must be subjected to a searching examination before they can yield serviceable results. The method of measuring the pressure forms the chief obstacle to the closer verification, as was remarked p. 407. Hitherto this method consisted in observing the diminution of volume of a given quantity of a so-called permanent gas (either air, nitrogen, or hydrogen) supposed to follow Boyle's law. The compressibility of nitrogen, however, has been investigated by Cailletet and Amagat, the pressure being directly measured by mercury (Cailletet, *C. R.* lxxxviii. p. 61, 1879; Amagat, *C. R.* lxxxix. p. 437, 1879, *Beibl.* iii. p. 253, and iv. p. 19; Roth, Wied. *Ann.* xi. p. 1, 1880). Their results, however, are not sufficiently concordant to give a measure of pressure accurate enough for our purpose. Andrews (Phil. Mag. [5] i. p. 78, 1876, *Beibl.* i. p. 21, 1877) extended the above investigations on carbonic acid to higher temperatures; but the agreement of his results with our equation must be pronounced much less satisfactory. Besides, it is not quite clear whether hydrogen or air was used to measure the pressure; and these gases for comparison with mercury pressures need quite opposite corrections.

Janssen ("Stickstoffoxydule in den vloebaren en gasf. toestand.," *Inaug.-Dissert.*, p. 50, Leyden, 1877; *Beibl.* ii. p. 136, 1878) has investigated nitrous oxide with Andrews's apparatus, and has fixed the data of the critical point in a specially careful manner. From this it follows, as will be explained below, that $a=0·00742$ and $b=0·00194$. Thus the equation for this gas becomes

$$\left(p+\frac{0\cdot00742}{v^2}\right)(v-b)=1\cdot00742\,(1-b)(1+\alpha\,t).$$

Proceeding with Janssen's observations as we did with Andrews's, we get the values of b from p (in atmospheres), together with the volume v. The following Table gives the values :—

25°·15.			23°·2.		
p.	$v.10^5$.	$b.10^5$.	p.	$v.10^5$.	$b.10^5$.
51·50	1383	189	45·11	1862	179
57·85	1056	189	47·85	1716	177
59·44	744	195	51·29	1539	178
62·30	403	188	55·70	1324	177
			57·40	1241	180

38°·40.			43°·8.		
55·34	1449	185	65·19	1154	85 N.B.
70·86	869	102	73·15	910	193
73·49	785	195	80·80	684	197
75·13	711	196	84·37	555	197
76·72	647	196	90·03	402	190

The value marked N. B. may probably be ascribed to a faulty observation or calculation, considering the remarkable agreement in the other places. The following tables give a set of values which were obtained for carbonic acid and ethylene by an apparatus quite similar to Andrews's (Roth, Wied. *Ann.* xi. p. 1, 1880). No correction has been considered necessary for the volume of air or nitrogen used to measure the pressure, just as no correction was used for Janssen's values in the case of nitrous oxide. For ethylene Van der Waals found $a=0\cdot00786$ and $b=0\cdot00224$ from the critical pressure (58 atm.) and the critical temperature (9°·3). The calculation is founded on this value of a.

Carbonic Acid.

49°·5.		
p.	$10^5 . v$.	$10^5 . b$.
20	5442	263
30	3405	240
40	2443	268
50	1846	287
60	1419	268
70	1248	290
80	881	264
		Mean... 269

99°·6.			183°·8.	
p.	$10^5 . v$.	$10^5 . b$.	$10^5 . v$.	$10^5 . b$.
20	6535	306	8199	297
25	5146	294	6515	297
30	4194	267	5410	296
35	3544	271	4603	290
40	3072	284	3999	297
45	2723	300	3528	293
50	2415	302	3185	293
55	2176	305	2890	318
60	1950	300	2629	293
65	1752	283	2377	285
70	1601	281	2167	267
75			2008	266
80		Mean... 290	1873	269
85			1756	271
				Mean... 288

Ethylene.

18°.			50°·2.		
p.	$10^5 . v.$	$10^4 . b.$	*p.*	$10^5 . v.$	$10^4 . b.$
15·63	6400	26	17·50	6400	25
16·50	6000	24	18·53	6000	25
18·15	5400	24	20·35	5400	23
19·40	5000	24	21·85	5000	23
21·75	4400	25	24·60	4400	24
23·75	4000	25	26·85	4000	25
27·05	3400	21	30·80	3400	21
29·65	3000	21	34·40	3000	23
32·90	2665	23	42·15	2368	25
39·20	2132	24	53·15	1776	25
48·50	1599	25			

99°·6.			182°·8.		
20·50	6400	26	25·70	6400	29
21·65	6000	24	27·50	6000	32 ?
24·00	5400	23	30·15	5400	28
25·85	5000	26	32·55	5000	28
28·80	4400	22	37·00	4400	29
32·50	4000	32 ?	40·20	4000	26
36·90	3400	23	47·45	3334	26
41·40	3000	25	52·80	3000	27
57·75	2050	25	62·05	2508	26

Almost everywhere there is an increase in *b* with rise of temperature ; but more accurate investigations are necessary before we can form a decisive judgment on this point.]

(e) *Critical Temperature.*

The following question obtrudes itself on us :—Why is it, in the case of carbonic acid, that below 30°·9 some volumes seem impossible, while above that temperature all volumes are equally possible? The following considerations are intended to furnish an answer to this question, and at the same time to illustrate the most satisfactory application of our equation.

Let us consider the curve denoted by

$$\left(p+\frac{a}{v^2}\right)(v-b)=(1+a)(1-b)(1+\alpha t),$$

when t is constant, and v, p are abscissa and ordinate respectively. Thus the curve is an isothermal. Neglecting a and b, the curve is an equilateral hyperbola, and this has hitherto been regarded as the isothermal of so-called perfect gases. But we saw that the constants could not be considered zero for carbonic acid, nor for air nor hydrogen. For a given p the curve gives a cubic equation for v, which is a remarkable property. Such an equation, as is known, has either one or three real roots. Consequently a right line parallel to the volume-axis cuts the curve either in one or three points. In other words, at a given pressure and temperature there are either three volumes possible or else only one. The result that, at a given temperature, there are three volumes possible certainly seems strange. For some values of t we know the substance in the liquid and in the gaseous state; but to what state can the third volume correspond? It certainly cannot be considered as the volume which the body assumes in the solid state, this being quite outside our considerations. We shall see immediately that the third volume is greater than the liquid and less than the gaseous volume. It is only requisite to trace one such isothermal (*e. g.* that for 13°·1) to see the relations clearly (Plate V. fig. 1). Taking p equal to the pressure of the saturated vapour at this temperature, or equal to the pressure under which the liquid and its vapour continue in equilibrium together in a given space, it appears that the third volume corresponds to that part of the isothermal for which $\frac{dp}{dv}$ is positive. The theoretical possibility of this volume is thus indicated; but at the same time it is indicated that the substance is then in unstable equilibrium. If we imagine for a moment that this volume condition is realized, then, by an infinitely small diminution of volume, a state will ensue which will require a pressure only slightly less than the pressure really present, and consequently the substance will assume the smaller liquid volume explosively.

Though, so far as I know, the theoretical proof of the existence of the third volume condition has not been hitherto given, it has been conjectured by James Thomson (Maxwell, 'Theory of Heat,' p. 125), who conceived the happy idea of constructing the part of the isothermal belonging to volumes beyond the reach of experiment by means of the part of the isothermal given by experiment; and the curve thus resulting is quite analogous to that deduced from my equation. (See the paper of James Thomson in the 'Transactions of the British Association,' 1871, p. 30.)

In order to show this agreement graphically I have taken from Maxwell the curves, Plate V. figs. 2 and 3, and contrasted them with fig. 1, which gives my isothermal *.

Consider the part H G C B A of an isothermal for any temperature below 30°·9. Experiment gives us data for all the part to the right of G and to the left of C. The idea of joining C and G by a straight line, as is done by Maxwell, is not a happy one; Thomson's curve G F E D C is drawn beside it. The point E gives the magnitude of the third volume possible at this pressure and temperature (the isothermal chosen was drawn for 13°·1) †.

From the foregoing table the vapour volume denoted by G is equal to 0·012332, and the liquid volume denoted by C is equal to 0·0022647. The third root of our equation gives the point E.

We can fix the limits within which E must lie by means of the equation

$$\frac{dp}{dv} = -\left\{\frac{(1+a)(1-b)(1+\alpha t)}{(v-b)^2} - \frac{2a}{v^3}\right\}.$$

For very great values of v, this expression is evidently

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* In fig. 1 a pressure of 1 atmosphere is represented by 1 mm., and b by 10 mm.; the isothermal drawn is that for 13°·1.

† [The experimental data, however, are accurately embodied in what Van der Waals calls Maxwell's curve; and this involves no "idea" whatever—either fortunate or the reverse.—*Note by the English Translators.*]

negative; for values of v between the two greatest roots which make $\frac{dp}{dv}=0$ it is positive; and for values of v between the two least roots it is again negative. The portion of the curve lying between the points corresponding to the two greatest roots will represent an impossible state. In the figure these points are represented by the points D and F. By substitution in the original equation, they give a maximum and a minimum pressure.

We find these two roots of $\frac{dp}{dv}=0$ equal to 0·0085 and 0·0056 approximately, and the third volume is between the two. But it is only between the maximum and the minimum pressure that a line parallel to the axis of v cuts the isothermal in three points. At pressures below the minimum and above the maximum pressure, only one volume is possible. In the first case it is a volume of vapour, and in the second case a volume of liquid.

It seems surprising that a liquid volume should be possible at a pressure less than that of the saturated vapour. But it will not seem so strange on considering the experiments of Donny and others.

Liquids free from air in exhausted vessels can be heated to very high temperatures without boiling, if only one end of the vessel be kept cold. Here we have liquids persisting under a pressure less than the maximum pressure of the vapour at the temperature they actually reach. The volume of the liquid under this condition of diminished pressure is of course greater than it is under ordinary conditions at the same temperature. The point D, whose position is given by $\frac{dp}{dv}=0$, gives the greatest liquid volume possible at the given temperature; and the minimum pressure represented by D is the lowest pressure at which the liquid can remain liquid. The isothermal here chosen—that for 13°·1—does not allow of the pressure for liquid carbonic acid ever becoming zero. It is, however, an interesting question whether this is possible at other temperatures—a question, in fact, which could scarcely be answered without the help of our equation.

Putting $p=0$, and solving for v, we find

$$v=\frac{a}{2(1+a)(1-b)(1+\alpha t)}\pm\sqrt{\frac{a^2-4ab(1+a)(1-b)(1+\alpha t)}{4(1+a)^2(1-b)^2(1+\alpha t)^2}},$$

besides $v=\infty$, which is omitted.

If v is to be real, then we must have

$$a > 4b(1+a)(1-b)(1+\alpha t);$$

or the maximum temperature at which this is possible must be given by

$$1+\alpha t=\frac{a}{4b(1+a)(1-b)};$$

leading to

$$v=2b.$$

That is at about −16° and at a volume of about 0·0046—just the volume down to which our equation gave constant values of b. We shall show presently how the maximum value of t may be arrived at without a knowledge of a and b. At lower temperatures than that here determined, the pressure becomes negative between the two values of v for which the pressure vanishes.

The part of the isothermal lying between G and F remains to be discussed. We have, in fact, to consider whether it is possible for the vapour-pressure to attain a greater value than that which is ordinarily termed the maximum vapour-tension. Though this question is more difficult than the previous one, there is some ground for answering it in the affirmative. The maximum pressure of the vapour is not absolutely constant. It not only depends on the vapour itself, but on the liquid present in the same space. Thus the maximum vapour-pressure over water in which salt is dissolved is less than that over pure water. Even the form of surface of the liquid influences the pressure of the saturated vapour. W. Thomson (Maxwell, 'Theory of Heat,' p. 267) has shown that over a capillary concave surface the pressure is less, and over a convex surface greater, than it is over a plane liquid surface. Thus, in a space whose walls are quite dry, and in which rather small liquid drops are alone present, the pressure is greater than the maximum pressure as ordinarily given. By the evaporation of such drops the pressure can be brought to its greatest possible value.

[*Addition by the German Translator.*—In a discussion on the behaviour of carbonic acid (Wied. *Ann.* ix. p. 337, 1880), Clausius makes some remarks which are not without interest in reference to the relation of the bent portion of the isothermal H G F E D C B theoretically indicated, to the straight line G E C corresponding to the actual process. Between the two states of the substance indicated by the points G and C there are two ways by which the substance can pass from one state to the other. We may regard the combination of these paths as a reversible cyclic process; and therefore the equation

$$\int \frac{dQ}{T} = 0$$

must hold, where dQ denotes an element of heat supplied from without, or given up. Here T is constant: so the equation simplifies to

$$\int dQ = 0.$$

Hence it follows that the positive and negative parts of the external work done during the cyclic process must cancel. Now, since the surplus of the positive over the negative work corresponding to each portion of the cyclic process is represented by the area between the right line and the curve, the area above the right line representing a positive surplus and the area below a negative surplus, it follows that these two areas must be equal.]

Supplementary Note by the Author.—The equality of these spaces was first enunciated by Maxwell ('Nature,' 1875). Maxwell's proof rests on the axiom that no interchange of heat takes place between two bodies at the same temperature. The proof given by Clausius rests on the Second Law of Thermodynamics. Both proofs apply a principle derived from experience to a case which cannot be realized by experiment, and must therefore in so far remain doubtful. Maxwell's position is, however, stronger than that of Clausius. A proof of the equality of the curve spaces can also be derived from the theorems of Gibbs on the thermodynamic surface (Gibbs, "On the Equilibrium of Heterogeneous Substances").]

Let us now investigate the effect of increased values of t, by a further consideration of the details of the isothermals.

The limits between which at 21°·45 imaginary values of v occur, are, for the points D and F of the isothermal,

$$v_1 = 0{\cdot}008 \quad \text{and} \quad v_2 = 0{\cdot}006.$$

For isothermals corresponding to higher temperatures these roots approach each other, and become imaginary for the isothermal of 31°. Thus, in this isothermal the curved part F E D C B disappears, and no line parallel to the v-axis can cut the curve in three points. In order to find the temperature at which this sort of isothermal commences, we must determine what values of p and t in the original equation lead to an equality of the three roots.

Writing the original equation

$$v^3 - \left\{ b + \frac{(1+a)(1-b)(1+\alpha t)}{p} \right\} v^2 + \frac{a}{p} v - \frac{ab}{p} = 0,$$

if x is the threefold root, then

$$3x = b + \frac{(1+a)(1-b)(1+\alpha t)}{p},$$

$$3x^2 = \frac{a}{p},$$

$$x^3 = \frac{ab}{p},$$

or

$$x = 3b, \qquad p = \frac{a}{27b^2},$$

$$1+\alpha t = \frac{8}{27} \cdot \frac{a}{1+a} \cdot \frac{1}{b(1-b)}.$$

The signification of this temperature—the Critical Temperature of Andrews—is clear from what precedes. Below it a substance can exist in the so-called gaseous as well as in the so-called liquid state, according to the external pressure. At certain pressures the substance may assume either state ; but above the temperature in question it can exist only in one, whatever be the pressure. When the temperature is above the critical, it is useless to try to liquefy the substance. The honour of this remarkable discovery, which alters our views as to the so-called permanent gases, and the liquefaction of gases generally, belongs to Andrews *.

That it was not so easy to reach this conclusion from experiments appears, amongst other circumstances, from Regnault giving in good faith maximum pressures for carbonic acid above 40°. Certainly Regnault carried on his experiments in metallic vessels, and thus could not perceive the actual process.

That the prevailing views on the liquefaction of gases need correction is shown by the very phrase "Condensation of Gases." In this phrase, condensation is evidently regarded as depending on the volume. So the customary assertion that a gas becomes liquefied by pressure, and that cooling (which really diminishes pressure) promotes this liquefaction, must be just reversed. A gas may become liquid by cooling without any remarkable pressure being required. Even Regnault appears to have had no real conception of this view of the liquefaction of gases, as we may see from his own words:—"Par la quantité d'acide carbonique, que l'on a fait sortir de l'appareil à la fin des expériences, on a reconnu, que même à la température de +40°, il devait rester beaucoup d'acide carbonique liquide."

I consider that I have thus explained this hitherto inexplicable fact—at least if it can be called an explanation of a phenomenon, when it is shown to be a consequence of a universal physical law. By the three given equations we can express very simply the critical temperature, critical volume, and critical pressure, when the constants a and b for the substance are known. Experiment gives the critical temperature with sufficient accuracy. What I call the critical volume is the volume which is approached by a liquid under the pressure of its saturated vapour in the neighbourhood of the critical temperature. The critical pressure is the pressure at this limit. The two last quantities can be determined experimentally, although with more difficulty than the first.

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* [The idea seems to have occurred to Faraday. He ascribes the failure of his attempts to liquefy air to the too high temperature. Little regard, however, seems to have been paid to this. (See *Fortschr. der Phys.* 1845, p. 130.) Faraday also conjectured, especially in the case of carbonic acid, the occurrence of the "Cagniard de la Tour state," which occurs in this case at 90° F.=32 ·2 C. (Compare Pogg. *Ann.* Ergbd. ii. p. 210, 1848.).—*Note by the German Translator.*]

The critical temperature is given by

$$1+\alpha t=\frac{8}{27}\,\frac{a}{(1+a)(1-b)b};$$

and when $a=0{\cdot}00874$ and $b=0{\cdot}0023$, we get the value 32°·5. The result is very satisfactory, especially when we consider that an error in the ratio $\frac{a}{b}$ produces in t an error nearly 100 times greater. If, conversely, from $t=30°{\cdot}9$ we had found the ratio of a to b, we should have got $b=0{\cdot}0023$ again, when $a=0{\cdot}00874$. We shall use the critical temperature in this manner. It gives, very approximately, the value $\frac{27}{8}(1+\alpha t)$ for the ratio $\frac{a}{b}$. According to Andrews, the critical volume for carbonic acid at 31°·1 is $\frac{1}{169}$ of the volume at that temperature and under one atmosphere pressure, and is therefore about 0·0066; hence $b=0{\cdot}0022$.

The values for the pressure we should expect to be less satisfactory. From $p=\frac{a}{27b^2}$ it should be about 61 atmospheres, while observations of the manometer showed that the air was compressed to $\frac{1}{73}$, and therefore that the pressure was about 70 atmospheres. Perhaps this apparently great difference between 61 and 70 atmospheres is to be ascribed to the small quantity of air dissolved in the carbonic acid, which at all events must produce a diminution of the constant a. Now the value $\frac{a}{v^2}$ amounts to more than 200 atmospheres for this value of v. If the critical pressure p is really 70 atmospheres, the molecular attraction would have to be 191 atmospheres, and this would lead to the value 0·00835 for a. The variation of a caused by the small quantity of air present can scarcely be so great as to account for this difference. But in any case the presence of the air has some effect. Observation of the phenomena of the critical point has not hitherto yielded us a sufficiently firm basis for the deduction of the instantaneous condition of the substance; but we are enabled to decide as to the trustworthiness of the observations in general by examining one of the phenomena more particularly.

By eliminating a and b we get approximately

$$\tfrac{3}{8}(1+\alpha t)=pv. \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mu)$$

The left-hand side of this equation has the value 0·4174, and when $v=0·0066$ we get $p=63·3$ atmospheres.

The more accurate equation is

$$\tfrac{3}{8}(1+\alpha t)=\frac{pv}{(1+3pv^2)\left(1-\frac{v}{3}\right)}, \quad . \quad . \quad . \quad (\nu)$$

which gives $p=63·5$ atmospheres. Although here the value of p is nearer to that given by experiment, yet there must have been some disturbing influence at work.

Equation (μ) shows further that at the critical point the density is nearly $\frac{8}{3}$ times greater than that given by Boyle's and Gay-Lussac's laws. The experiments of Cagniard de la Tour, who as early as the year 1822 demonstrated the possibility of this state for ether, alcohol, carbon bisulphide, water, &c., will serve in a certain sense as a test of the truth of these consequences of our theory (*Ann. de Chim. et de Phys.* xxi. p. 178, xxii. p. 413).

We may consider that the critical temperature was pretty accurately determined by Cagniard de la Tour; though we must regard it as purely accidental if the critical volume was the volume really examined. The method adopted was analogous to Bunsen's method of determining the effect of pressure on the melting-point of certain bodies. Consequently the volume of the body at the critical temperature depended altogether on the quantity of liquid accidentally present. From the first table (*loc. cit.* xxii. p. 411) we see that when the original volume of liquid ether was 7, the volume of the vapour was 20. Expressed in our units, this gives the vapour volume $=\frac{20}{7}\times 1·41\times\frac{1}{302}=0·01334$. The pressure was 37·5 atmospheres, thus $pv=0·5$. The critical temperature being 187°·5, we have $1+\alpha t=1·686$. Hence $\frac{pv}{1+\alpha t}=0·3$; our equation would give 0·375. In a second experiment with a different quantity of ether, the vapour volume was 0·02668 and the pressure was 42 atmospheres, just the reverse of the other experiment. Hence we get pv

$=1{\cdot}12$ and $\frac{pv}{1+\alpha t}=0{\cdot}66$. Since in the second experiment the volume was twice as great as in the first, we see that Cagniard de la Tour's experiments in themselves give little information as to the critical volume. On the other hand, the critical pressure can be estimated at least approximately; for at the critical point the isothermal runs parallel to the axis of volume, so that a considerable error in v will cause only a small error in p. If from $t=187^\circ{\cdot}5$ and $p=37{\cdot}5$ we calculate the values of a and b, we find $a=0{\cdot}027$ and $b=0{\cdot}005$. Consequently the critical volume is $0{\cdot}015$. Thus the volume first observed was too small and the second volume too great. And since, as we shall immediately show, the product pv at the critical temperature must continually diminish until $v=2{\cdot}2b$, it should not surprise us to find pv in the first experiment too small and in the second too large.

For carbon bisulphide we find (*loc. cit.* xxii. p. 413) $t=262^\circ{\cdot}5$ and $p=78$. Hence $a=0{\cdot}022$ and $b=0{\cdot}0032$. Also the critical volume $=0{\cdot}0096$. Cagniard de la Tour gives 20 as the vapour volume in the experiment, and 8 as the liquid volume; or in our units the vapour volume is denoted by $\frac{20}{8}\times 0{\cdot}81\times\frac{1}{291}=0{\cdot}007$. Here again the volume is smaller than the critical volume, consequently we may expect that pv will be less than $0{\cdot}375\ (1+\alpha t)$, and, in fact, we find it equal to $0{\cdot}276\ (1+\alpha t)$. That Cagniard chose volumes which were always smaller than the critical volume (with one exception, where he intentionally chose a volume greater than it) may perhaps be accounted for by his filling the apparatus just so full as not to burst it at the critical temperature. It appears from the shape of the isothermal that for volumes less than $3b$ the pressure will rise so rapidly that there is some danger of bursting the vessel.

By means of the critical temperature we can also find a simpler expression for the maximum temperature at which a liquid can exist under zero pressure; that is, under the condition of the molecular attraction being in equilibrium with the opposing forces due to the heat-motion. With the object of securing this condition we must prevent evaporation from the free surface of the air-free liquid by covering it with a layer of oil, or by some other suitable method. We saw above that the pressure will be zero for a temperature given by

$$1+\alpha t=\frac{a}{4b(1+a)(1-b)};$$

and that then the volume will be equal to $2b$.

Calling the critical temperature t_1 and the temperature required t_2, we find

$$1+\alpha t_2=\frac{27}{32}(1+\alpha t_1).$$

For carbonic acid this gives $t_2=-16°$ nearly. For water with a critical temperature of 412° we get $t_2=325°$.

Observations of air at high pressure have also been made by Cailletet. These confirm the correctness of our equation, and at the same time lead to some important consequences. Cailletet gives for each pressure the value of the product of the pressure and volume, taking as unity that product which the air used in the experiments gave at 15°. This product of course diminishes, but not indefinitely. Cailletet finds a minimum value for it between 60 and 80 atmospheres. Let us examine whether this can be deduced from our equation.

From

$$p=\frac{(1+a)(1-b)(1+\alpha t)}{v-b}-\frac{a}{v^2}$$

we get

$$pv=(1+a)(1-b)(1+\alpha t)\frac{v}{v-b}-\frac{a}{v},$$

and

$$\frac{d(pv)}{dv}=-(1+a)(1-b)(1+\alpha t)\frac{b}{(v-b)^2}+\frac{a}{v^2}=0,$$

or

$$\frac{v^2}{(v-b)^2}=\frac{a}{b(1+a)(1-b)(1+\alpha t)}. \quad . \quad . \quad . \quad (\pi)$$

If p is expressed in atmospheres and v in terms of the volume assumed by the air at $t°$ under one atmosphere of pressure, then $a=0{\cdot}002812$ and $b=0{\cdot}00197$; hence $\frac{v}{v-b}=1{\cdot}16$ approximately, or $v=7{\cdot}25b=0{\cdot}014326$. Hence we get $p=72$ atmospheres.

At a still higher pressure Cailletet finds the product again equal to unity. In order to find the pressure at this point, write the equation

$$pv+\frac{a}{v}-bp-\frac{ab}{v^2}=(1+a)(1-b)(1+\alpha t).$$

If in this we put $pv=(1+a)(1-b)(1+\alpha t)$, we should find for p approximately the same value as Cailletet did when $pv=1$. Doing so we get

$$\frac{a}{v}-\frac{ab}{v^2}=bp=\frac{b(1+a)(1-b)(1+\alpha t)}{v},$$

or $v=3\cdot84b$ and $p=140$ atmospheres.

Cailletet observed that pv was equal to unity at about 180 atmospheres. The discrepancy is indeed great, but since the measurement of the volume at high pressures is liable to a greater relative error we cannot expect any very close agreement with our calculation, even assuming the accuracy of our constants.

The observations published by Amagat in 1879 on the compressibility of gases at high pressure (*C. R.* lxxxix. pp. 437–439, 1879; *Beiblätter*, iv. p. 19, 1880) confirm the accuracy of our equation for air, as the following table shows. The pressure p is expressed in metres of mercury, and column I. contains the calculated value of pv multiplied by 10^3, while column II. contains the observed value of pv multiplied by 10^3.

p.	I.	II.	p.	I.	II.	p.	I.	II.
1	1	1	45·24	......	978	78·67	984	......
9·94	994	......	48·86	977	......	84·22	......	980
19·77	998	......	55·50	......	977	89·03	989	......
24·07	......	984	58·64	977	......	99·85	998	......
29·53	984	......	64·00	......	977	101·47	......	990
34·90	......	982	68·55	979	......	111·09	1009	......
39·25	981	......	72·16	......	978	133·89	......	1009

According to these observations the minimum value of pv occurs when $p=80$ atmospheres, and a change of sign should occur when $p=150$ atmospheres.

In the case of hydrogen Cailletet finds for pv constantly increasing values, and this corresponds with Regnault's observations. Since for hydrogen we saw that a was almost zero and much less than b, neither a maximum nor minimum value of pv can exist. Thus, in order to satisfy equation (π), it would be necessary to have $v<v-b$. Previously we got 0·00065 as the value of b for hydrogen ; in the units we are working with at present this becomes about 0·00049. Now, Cailletet observed that the product pv at 100 atmospheres was $\frac{1}{0{\cdot}9552}$, whence $b=0{\cdot}00047$. At 250 atmospheres the product is $\frac{1}{0{\cdot}9001}$, whence $b=0{\cdot}00045$. At 605 atmospheres pv is $\frac{1}{0{\cdot}758}$, whence $b=0{\cdot}00053$. Thus we see that even at such enormous pressures the accuracy of the values of our constants for hydrogen are fully confirmed. At the same time the insignificance of a is very evident. The general equation for the volume at which pv is a minimum is

$$\frac{v^2}{(v-b)^2}=\frac{a}{b(1+a)(1-b)(1+\alpha t)}.$$

For the critical temperature the right-hand side of this equation is $\frac{27}{8}$; hence $v=2{\cdot}2\,b$. Consequently, at this temperature the phenomenon which Cailletet observed for air at the ordinary temperature, first occurs when the volume is sensibly below the critical volume. In order that the phenomenon may occur for values of v greater than $2\,b$, the temperature must satisfy the equation

$$\frac{v^2}{(v-b)^2}=\frac{27}{8}\cdot\frac{1+\alpha t_1}{1+\alpha t},$$

where t_1 denotes the critical temperature, or

$$1+\alpha t=\frac{27}{8}\cdot\frac{(v-b)^2}{v^2}(1+\alpha t_1).$$

When $v>2b$, then $\frac{(v-b)^2}{v^2}>\frac{1}{4}$,

or
$$1+\alpha t>\frac{27}{32}(1+\alpha t_1).$$

[*Addition by the German Translator.*—From the previous formulæ it follows that the minimum value of pv satisfies the equation

$$\frac{pv}{1+\alpha t}=(1+a)(1-b)\left\{2\sqrt{\frac{a}{b(1+a)(1-b)(1+\alpha t)}}\right.$$
$$\left.-\frac{a}{b(1+a)(1-b)(1+\alpha t)}\right\}$$

which, by using the equation for the critical temperature, becomes

$$\frac{pv}{1+\alpha t}=(1+a)(1-b)\left\{2\sqrt{\frac{27}{8}\cdot\frac{1+\alpha t_1}{1+\alpha t}}-\frac{27}{8}\cdot\frac{1+\alpha t_1}{1+\alpha t}\right\}.$$

If we take $t=t_1$ we get for pv the approximate minimum value 0·3.]

Amagat's values for ethylene in the treatise above cited have been applied by the author (Van der Waals, "Die Zusammendrückbarkeit des Aetheylens," *Versl. en Mededeel. der k. Ak. van. Wet.*, Afd. Natuurk. [2] xv. 1880; *Beiblätter*, iv. p. 704, 1880) to the verification of the given relation. For this purpose it was necessary to determine experimentally the critical point of ethylene; by means of Cailletet's pump the critical pressure was found to be 58 atmospheres, and the critical temperature 9°·3. It will be noticed that of all gases ethylene has the most easily determined critical point. From the data thus obtained we may by our former method (p. 420) find the values of a and b. These are $a=\cdot 0101$, $b=\cdot 0029$. If p is the pressure expressed in metres of mercury, the equation of condition for ethylene becomes

$$p=\frac{1\cdot 0072(1+\alpha t)}{v-0\cdot 0029}-\frac{0\cdot 0101}{v^2}.$$

Baynes (Nature, xxii. p. 186, 1880), using the values for the critical point given by the author, has compared our formula with the numbers obtained by Amagat for ethylene, and gives in atmospheres

$$p=\frac{0\cdot 0037(272\cdot 5+t)}{v-\cdot 00224}-\frac{\cdot 00786}{v^2}.$$

We abstract the following Table of comparison from Baynes's paper, p being still expressed in atmospheres.

Column I. contains the values of vp obtained from Amagat divided by 23500; column II. the corresponding numbers obtained from the formula for a temperature of 20°. The values in columns I. and II. are multiplied by 10^3.

p.	I.	II.	p.	I.	II.
31·58	914	895	133·26	520	520
45·80	781	782	176·01	643	642
59·38	522	624	233·58	807	805
72·86	416	387	282·21	941	940
84·16	399	392	329·14	1067	1067
94·53	413	413	398·71	1248	1254
110·47	454	456			

The agreement is certainly very satisfactory. The discrepancy in the third set is attributed by the author to a typographical error in Amagat's table. The minimum value of pv does not descend to the value at the critical temperature given above as ·3.

Returning to the general argument, we see that the smallest value of t for which pv can reach a minimum at volumes greater than $2b$ is consequently identical with the highest temperature at which a substance can exist without external pressure. But the minimum is first reached at the critical temperature when $v = 2{\cdot}2b$; and for lower values of t we have correspondingly lower values of v. All such values, however, below the critical temperature must, according to our theory, be impossible; or, at least, must correspond to a substance in its liquid state. Consequently, we may define the critical temperature as the lowest temperature at which minimum values of pv can actually be observed.

Above its critical temperature every substance has a right to the title "Permanent Gas." A stronger claim still to the title have those gases which have not yet been liquefied; but they must not be treated as *par excellence* the five permanent gases. At temperatures above 30°·9 carbonic acid shares all their honours. The critical temperature of air cannot differ much from $-158°$, nor the critical pressure from 24·5 atmospheres. Though this pressure lies well within experimental reach, the temperature up to date does not. For hydrogen the critical temperature cannot be much higher than $-273°$. That the constant a is insensible for hydrogen does not imply that it is of true zero value; on the contrary, we must under all circumstances allow the property of attraction to matter.

Finally we are left with the question : When can we call a substance liquid and when gaseous? After all that has been said no one will be found to assert that there is a discontinuous transition from one state to the other. We have, in fact, shown that the two states may be treated in one and the same equation.

Neither density nor pressure enters into the question ; the form of the molecular motion and the magnitude of the molecular forces may be of the same order in both conditions of matter. It must therefore be possible to convert a quantity of vapour into a quantity of liquid in a perfectly continuous manner. Consider a quantity of carbonic acid at a temperature of 13°·1 and at a pressure less than the maximum vapour tension ; let the volume be diminished ; at a certain point there is a sudden change, and finally the whole volume of gas is converted into a perfectly definite volume of liquid. Let us heat such a gas at constant volume to a temperature above the critical—during which process it obviously remains a gas—and then diminish the volume till it finally reaches the volume which would be occupied by the liquid. It still will remain a gas, since it is above the critical temperature. Keeping the substance at this diminished volume, let it be gradually cooled ; no sudden change of state results—the substance remains homogeneous throughout its whole bulk. Now, we cannot but call this substance a gas, though formerly we called it a liquid. I have borrowed this remark from Maxwell.

The equation

$$p_t - p_0 = \frac{(1+a)(1-b)}{v-b} \alpha t.$$

gives a means of constructing the different isothermals. If one isothermal is constructed and one point of a second is known, then all the remaining isothermals can be simply determined.

CHAPTER IX.

Values of K.

We may now pass on to determine approximately for some substances the values of the constant K, which occurs in Laplace's theory of Capillarity. This quantity K is the attraction exerted inwards on the surface layer; and thus it is known when a and the volume are given. We shall express it in atmospheres, as is done by Laplace. Owing to the fact that carbonic acid has a critical temperature and pressure which are easily attainable, a considerable number of experiments have been made on this substance, and from them, as we have seen, only a rather rough value of a could be obtained. Most substances, however, do not lend themselves to investigation so easily as carbonic acid, and in consequence the appropriate values of a are in these cases even less reliable. Several values of K will be found in the sequel; these are not given with any conviction of their accuracy, but because I consider it as well to make some kind of beginning in the direction of their determination. In consequence of our hitherto complete ignorance of the real magnitude of the quantities involved, no really trustworthy conjecture has as yet been based on any probable grounds. Laplace (*Méc. Cel.* bk. 10, 2nd suppl.) has advanced a hypothesis, but arrives at a result which he himself regards as improbable. By supposing the attraction of water on water to be equal to the attraction of water on light, or rather on the corpuscles supposed to produce it, he finds for K the weight of a column of water whose height is 10,000 times the distance of the earth from the sun. According to our present views as to refraction of light, this statement can only be regarded as a curiosity. Laplace, however, was quite right in making K almost infinitely greater than H.

Some causes of inaccuracy in determining the values of K, even supposing a to be accurately known, may be found in possible changes of the molecular extension due to changes of temperature. At first we regarded the temperature as affecting b only, but evidently it must also have an effect in increasing or diminishing the distance to which the centres of the molecules approach each other during their motion, because of the variation in size of the molecules themselves. Consequently, the attraction cannot be the same as before; and the change in the attraction for the highest degrees of density, where the number of the encounters has so greatly increased, must become much more important than for the volumes hitherto considered.

For carbonic acid we found $a=0{\cdot}00874$ atmospheres when the volume was about 509 litres per kilogram. At the greatest density attained by Andrews the volume of the same weight of carbonic acid became $0{\cdot}00205 \times 509$, or 1·083 litres. The carbonic acid had about the density of water, and the molecular volume was $0{\cdot}0023 \times \frac{509}{4} = 0{\cdot}307$ litre. In order to be able to judge of the degree of condensation we must compare the apparent volume with the volume taken up by the molecules, and regard the substance as denser when v is a smaller multiple of b. If now, as is very probable, the molecular volume of a kilogram of water be greater than that of a kilogram of carbonic acid, then, even if the apparent volumes are equal, we ought to call the water more condensed than the carbonic acid, as will be clear from what follows. We found smaller values of b for bodies of smaller molecular weight; these values, however, were not expressed in absolute units; they denoted rather a fractional part of the volume assumed by 1 kilogram under 1 atmosphere pressure. This last volume is in the case of most gases inversely proportional to the molecular weight. If, now, the above values of b were proportional to the molecular weights, then it would follow that the molecules in 1 kilogram of all bodies would occupy the same fraction of a litre. But we found values of b approximately proportional to the square root of the molecular weights; thus we arrive at the conclusion that the molecules in 1 kilogram occupy a comparatively greater volume the lighter they are. Consequently, as already said, water is more condensed than carbonic acid, the external volume being the same for each.

For liquid carbonic acid everything points to the validity of the equation $\mathrm{K}=\frac{a}{v^2}$. When the volume was diminished nearly 500 times we found the value of K to be 2180. At the critical volume, which is the greatest volume possible in the liquid state, we should naturally get a much smaller value, and, in fact, it amounts to about 180 atmospheres only. By means of the constants we find the critical volume of air to be about 4·57 litres, and in this case the value of K becomes 72 atmospheres.

For ether, taking the values calculated from Cagniard de la Tour's data for the critical point, we find K=1310 atmospheres for the liquid volume at 0°, while the molecular volume $\frac{b}{4}$ is equal to 0·375 litre. Since the external volume is 1·36 litre it follows that at 0° and under the pressure of the atmosphere the density of ether is less than that of carbonic acid. The value 1310 atmospheres may consequently be received with some confidence, supposing the critical point to have been observed correctly by Cagniard de la Tour. However, as we previously remarked, it is uncertain whether the critical volume was the one really observed.

In the case of alcohol also, the observations of Cagniard de la Tour afford some data, which place the critical temperature at 256°, and the critical pressure at 119 atmospheres. It follows from this, by our equation, that $\frac{a}{b}=6·53$, and $b=0·00203$. Since the molecule of alcohol is $\frac{23}{22}$ times heavier than the molecule of carbonic acid, this would seem to be a case of a departure from the rule hitherto always confirmed, that b is greater for heavier molecules. We are, however, somewhat uncertain whether the alcohol used in these experiments was free from water and air, and therefore whether the observed was or was not greater than the true critical pressure; consequently, we need not lay much stress on this exception. I assume then, that in the case of alcohol, $b=0·0023$, giving by calculation $a=0·015$. These numbers make K=2330 atmospheres for the liquid volume at 0°. We should have got about 2050 atmospheres if we had used the values found by Cagniard de la Tour. From the value of b first chosen we get the molecular volume 0·247 litre, and from the second value we get the molecular volume = 0·28 litre.

Since the external volume is 1·234 litre, the condensation of alcohol is still less than that of ether.

Similarly for carbon bisulphide we are able to deduce a and b from the data of the critical point; we get $b=0·0032$ and $a=0·0022$. Since the liquid volume at 0° and 1 atmosphere pressure is nearly 352 times less than the vapour volume under the same circumstances, we get $K=2975$. For the molecular volume we get 0·265 litre*.

CHAPTER X.

Molecular Dimensions.

WE must now proceed to compare the quantity K with the second constant H, which Laplace introduced into his theory of Capillarity, and we shall see that some conclusions may be drawn from this comparison. We know the mathematical relation between the quantities in question. Thus, K represents

$$\int_0^\infty \psi(x)dx,$$

and H represents

$$\int_0^\infty x\psi(x)dx.$$

If $\psi(x)$ be considered to represent a force, then we may regard $x\psi(x)$ as the moment of this force with respect to the surface. Now since $\psi(x)$ diminishes continuously and rapidly between the values $x=0$ and $x=\rho$, where ρ is the radius of the sphere of action, we may put $H=x_1 K$, if we denote by x_1 a certain fraction of ρ. From knowing the capillarity we get the values of H for those bodies for which we have found K, as in the following table :—

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* The values of K for other substances are calculated in the 13th Chapter from later investigations, and are only referred to here for reasons which will appear later.

	K.		H.	
Ether	1300	atmospheres	3·7	milligram-millims.
Alcohol	2100	,,	5·0	,,
Carbon Bisulphide	2900	,,	6·6	,,
Water	10500	,,	15·5	,,

If we express K in milligrams, taking one square millimetre as unit of surface, we get the following values of x_1 for the liquids mentioned above :—

Ether. . . . . $x_1 = \dfrac{3{\cdot}7}{13000000} = 0{\cdot}00000029$ mm.

Alcohol . . . . $x_1 = \dfrac{5}{21000000} = 0{\cdot}00000025$,,

Carbon Bisulphide $x_1 = \dfrac{6{\cdot}6}{29000000} = 0{\cdot}00000023$,,

Water . . . . $x_1 = \dfrac{15{\cdot}5}{105000000} = 0{\cdot}00000015$,,

Even if we take ρ as being several times greater than the values given above, it is still unlikely that the value of that quantity should reach those found—with, however, a certain amount of reservation—by Quincke. For instance, he makes $\rho = 0{\cdot}000050$ mm., and acknowledges himself that his result comes out considerably greater than he expected, and greater than ought to follow from our knowledge of capillary phenomena.

By aid of the above values of x_1 we are in a position to show that the molecular attraction becomes sensible, more especially when the surfaces are in contact. Thus, from the following calculations we shall find that x_1 can only be slightly greater than the distance between the centres of two molecules during an encounter.

For the mean path we get, by using Maxwell's factor $\sqrt{2}$, discussed p. 381, the value

$$l = \frac{\lambda^3 - \sqrt{2}\pi s^3}{\sqrt{2}\pi s^2}.$$

Here λ denotes the mean distance between the centres of the molecules, and s the distance at the instant of encounter.

Multiplying numerator and denominator by n, which represents the total number of molecules, and denoting the external volume by v, and four times the molecular volume by b, we get

$$l=\frac{v-\frac{3}{\sqrt{2}}b}{\frac{3}{\sqrt{2}}b}s.$$

For various bodies v and b are known, and thus we only require to know l in order to determine s from the last equation.

Maxwell (Phil. Mag. [4] xx. p. 31) has found $l=0{\cdot}00007$* for atmospheric air at 15° and under a pressure of one atmosphere. And we found above $b=0{\cdot}00197\,v$ under the same circumstances. Hence, $s=0{\cdot}00000027$ mm. approximately.

By means of the values of l and s for air we may endeavour to find them for other bodies in the following manner.

Let b_1 be four times the number of litres which the molecules of one kilogram of air occupy under the usual circumstances. If the number of molecules is n_1, then $\frac{b_1}{4n_1}$ is the volume of one molecule, whose linear dimensions are therefore proportional to $\sqrt{\frac{b_1}{4n_1}}$. If b_2 and n_2 denote the corresponding quantities for another body, then evidently

$$\frac{s_1}{s_2}=\sqrt[3]{\frac{b_1n_2}{b_2n_1}}.$$

Again, to the former degree of approximation

$$\frac{l_1}{l_2}=\frac{v_1s_1b_2}{v_2s_2b_1}$$

and

$$\frac{n_2}{n_1}=\frac{m_1}{m_2}=\frac{v_2}{v_1},$$

where m_1 and m_2 denote the molecular weights. Consequently

$$\left(\frac{l_1}{l_2}\right)^3=\frac{m_2{}^2b_2{}^2}{m_1{}^2b_1{}^2},$$

---

* [The value of l appears as ·000065 mm. from the paper quoted.]

or, if b is expressed not in litres, but as a fraction of the volume at 0° and 76 cm. pressure,

$$\left(\frac{l_1}{l_2}\right)^3 = \frac{b_2^2}{b_1^2}.$$

By this formula we can calculate the values of l for bodies for which b is known: thus

for Ether . . . . . $l = 0·00004$ mm.
for Carbonic Acid . . $l = 0·000063$ „
and for Alcohol . . . . $l = 0·000068$ „

whence we get s:—

for Ether . . . . . $s = 0·00000040$ mm.
and for Alcohol . . . . $s = 0·00000027$ „

It is certainly surprising to find s even at all greater than x_1. In all these calculations, however, we are only dealing with approximate values; and we have been altogether dependent on Maxwell's value of l for air *.

Moreover the result nowhere contains any absolute contradiction. During encounter the line joining the centres is only in exceptional cases perpendicular to the surface of the molecules. These results seem to me to justify the conclusion that the radius of the sphere of action is to be considered exactly equal to the distance between the centres of the molecules during encounter. Moreover, it is to be expected *à priori* that the attraction exerted by a molecule during encounter will surpass that exerted by it at the other distances considered. Accordingly we should not regard x_1 as a mean value only, and must in consequence simplify our original analytical expression by regarding a layer—of thickness equal to the radius of the sphere of action—as one single indivisible layer. By this I do not mean to say that there is no attraction at other distances, but that the attraction at this distance is so much greater, that it is alone necessary to consider it in the calculation.

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* [The above data do not require—on account of their only approximate character—any considerable rectification from the later determinations of Puluj and Obermayer. See O. E. Meyer: *Kinetische Theorie der Gase*, p. 140.—*Note by the German Translator.*]

Though this result may sound surprising, it was in a certain measure to be expected; and in particular serves to show us how ill-founded was the original conception of the so-called permanent gases.

According to this result, molecular forces have sensible values even when the volume is somewhat great, and this is to be ascribed to the intimate approach of the molecules brought about by their motion. Further, since the number of encounters in any given fraction, even in the surface layer, of a volume of any substance is proportional to the square of the density (Maxwell, Phil. Mag. [4] xix. p. 27) this number is very much greater in very dense masses. If, therefore, we deny the existence of molecular forces in any gas, the encounters, and therefore the motion, must be considered as non-existent. This affords us quite a new standpoint from which to consider the meaning of the encounters. Hitherto they have been regarded as only opposing a diminution of volume; now they appear as producing an opposite effect in that they cause the exertion of a sensible attraction. In this there is no contradiction to our first supposition; on the contrary, there is additional light thrown on it. If we could have assumed this view *à priori* we should have been able to find the details of the isothermal curves more easily. This we could not do, and thus we had to try to reach our object by a longer way.

The determination of the value of b for any substance enables us to calculate the diameter, and therefore the absolute volume of a molecule; and at the same time the number of molecules in a given volume of the substance. Attempts have already been made to determine this number. Stoney (Phil. Mag. [4] xxxvi. p. 139) arrives at the result that for permanent gases under a pressure of one atmosphere the molecules occupy $\frac{1}{1000}$ part of the space in which the gas is contained. This result partly depends on an assumption made by Clausius (*Abhandlung* xv.). When Clausius speaks of the volume of the molecules, he means eight times their real volume. Stoney estimates the number of molecules in one cubic millimetre of gas at 0° and 76 cm. pressure at a million to the power of three, or 10^{18}.

Now using the value found for s in the case of air, viz.

0·00000027, we get the volume of a molecule considered as spherical to be

$$\tfrac{1}{6}\pi \times 0{\cdot}00000027^3 \text{ c. mm.};$$

and since we found the volume of all the molecules in 1 c. mm. to be $\frac{0{\cdot}001976}{4} = 0{\cdot}000494$ c. mm., it follows that the number of molecules is about 5×10^{16}, or about $\frac{1}{20}$ of the number obtained by Stoney. We must certainly admire the sagacity which, by a bold grasp of a simple supposition, arrives at a number of nearly the same order as that found by our calculations.

Stoney's method of calculation agrees with ours in a certain sense; but it differs from ours inasmuch as Stoney first endeavours to form a conception of the mean distance of the molecules under the given conditions, and thence derives the number of molecules; while, on the contrary, we derived the number in question from the magnitude of a molecule and the volume occupied by all the molecules. Conversely we can now easily determine the mean distance of the molecules supposed to be arranged in cubical order; it is

$$\frac{1}{\sqrt{50000000000000000}},$$

or about 0·0000025 mm. Stoney makes it 0·000001 mm.

The supposition of Clausius is consequently not quite confirmed by this result; we saw that eight times the volume of the molecules of atmospheric air occupies the $\frac{1}{250}$ part of the whole space taken up. I need scarcely again point out that the effect of this large fraction of the volume is opposed by the opposing influence of the attraction. It follows that Clausius, who disregarded the attraction, must have taken too small a quantity as representing the volume of the molecules.

Since all gases under the same conditions of temperature and pressure contain the same number of molecules in a given volume, the result found above for the mean distance, viz. 25×10^{-7} is of general application. The diameter of the molecules of air is $\frac{1}{10}$ of the mean molecular distance; but we know that the diameter of the molecules of other gases is not necessarily the same as for air, and therefore we cannot proceed to determine any general value for it. For instance, in the case of hydrogen the diameter is only $\frac{1}{15}$ at the mean distance.

Consequently it will never be possible to reduce a volume of air to the $\frac{1}{2000}$ part of the volume it would occupy under a pressure of one atmosphere. For hydrogen this limiting volume is $\frac{1}{3700}$ of the volume under one atmosphere pressure.

The absolute weight of a molecule of hydrogen is about 10^{-21} mg.

CHAPTER XI.

Application to Thermodynamics.

As an example of the value of our method of treatment of the theory of gases, we shall proceed to give some illustrations of its application to Thermodynamics.

It used to be thought that when a gas expands without doing external work, no temperature change ensues. The well-known experiment of Joule is considered to have established this theorem within certain limits, and it agrees perfectly with the prevailing belief that there is no molecular attraction in gases. But the foregoing considerations show that this cannot be the case. If the gas is so rarefied that the mean distance of the molecules far exceeds the greatest possible value of the radius of the sphere of action, still according to our views the quantity of potential energy possessed by the gas must diminish by rarefaction. There are always encounters between the moving molecules, but there are fewer the rarer the gas. During the period of approach, while one molecule is in the immediate neighbourhood of another, potential energy is lost. Thence it follows that up to very high degrees of condensation the quantity of potential energy lost is proportional to the density. This will be clear immediately if we consider that for each particle the number of encounters during a given time, at a fixed temperature, is proportional to the number of molecules present in the unit of volume. As the temperature increases the number of encounters becomes greater on account of the more rapid motion; but the period during which the molecules approach each other is diminished in the same measure. Hence might be drawn the conclusion, at least approximately, that the quantity of potential energy in a given quantity of gas does not depend on the temperature. If this be granted it is easy to see that the expansion of a gas, when there is no external work done, must be accompanied by cooling, since in the expanded condition less potential energy is lost in a given time; or, in other words, since expansion raises the potential energy. As early as 1854 Joule and W. Thomson gave the experimental proof of the truth of this consequence of our theory. In all gases, except hydrogen, cooling was observed. It is surprising that this fact has not long ago drawn attention to the difficulty of explaining the observed phenomena, even in permanent gases, unless molecular attraction is supposed to exist.

Our constant a plays the chief part in the calculation of the gain of potential energy by expansion. We see clearly that in gases this gain arises from the force exerted at the time of the encounters. We remarked before that we may regard this force as present only at the surface of the mass of gas, and this enables us more easily to obtain an expression for the work done against it. The force is of the form $\frac{a}{v^2}$, and therefore the gain of potential energy due to the increase of volume from v_1 to v is expressed by

$$\int_{v_1}^{v} \frac{a}{v^2} dv = a\left(\frac{1}{v_1} - \frac{1}{v}\right).$$

If there is any doubt as to the legitimacy of neglecting the forces within the mass, these may be easily taken into account, but the same result will be obtained. This immediately appears by considering the mass of gas in a cylindrical vessel of uniform cross section divided into horizontal layers. The lowest layer, considered as fixed during the expansion, attracts the second layer, this attracts the third, and so on. Thus during the expansion all the layers have their distances from each other increased; but the increase of the distance between two layers is only $\frac{1}{n}$th of the elevation of the upper surface of the gas, however great may be the number of layers denoted by n.

The sum of all the elementary quantities of work is thus exactly the same as if the attraction of the upper layer alone were considered in the calculation, and the displacement were the distance through which this layer is raised.

If the experiment could be carried on *in vacuo*, then the cooling of the gas would be equivalent to a gain of potential energy

$$a\left(\frac{1}{v_1}-\frac{1}{v}\right).$$

The calculation is somewhat more complicated for the experiment as arranged by Joule and Thomson. In this experiment a gas under high pressure p_1 is forced through a porous partition into a space at constant pressure p. If v_1 is the original volume, and v the volume at the pressure p, the work done on the gas is p_1v_1 and the work done by the gas is pv. If pv is greater than p_1v_1, there would be a cooling of the gas, which would have to be allowed for.

Let t_1 be the temperature when the volume is v_1, and t the temperature when the volume is v, where $t_1 > t$, then we have the two relations :—

$$pv+\frac{a}{v}-bp-\frac{ab}{v^2}=(1+a)(1-b)(1+\alpha t),$$

and

$$p_1v_1+\frac{a}{v_1}-bp_1-\frac{ab}{v_1^2}=(1+a)(1-b)(1+\alpha t_1).$$

The difference $pv-p_1v_1$ is very approximately

$$pv-p_1v_1=-(1+a)(1-b)\alpha(t_1-t)+\left\{\frac{a}{1+\alpha t}-b\right\}(p_1-p).$$

This gain of potential energy, together with the quantity gained within the mass, must be equivalent to the loss of heat of the gas by cooling.

In the above equation the unit of pressure is one atmosphere, and the unit of volume is the volume of the unit of weight of the gas at 0° and under a pressure of one atmosphere. In order to reduce the work to kilogram-metres, the above expression, understood to be for air, must be multiplied by $\frac{10334}{1{\cdot}293}$. Thus the gain of potential energy is altogether

$$-\frac{10334}{1{\cdot}293}(1+a)(1-b)\alpha(t_1-t)+\left\{\frac{2a}{1+\alpha t}-b\right\}\frac{10334}{1{\cdot}293}(p_1-p)$$

kilogram-metres; where p_1 and p are still expressed in atmospheres.

The kilogram of gas has been cooled through t_1-t degrees, and thus $c_1\,(t_1-t)$ calories has been given up, where c_1 denotes the specific heat of the gas for constant volume.

Thus we arrive at the following approximate equation:—

$$\left\{424c_1+\frac{10334\alpha}{1{\cdot}293}(1+a)\,(1-b)\right\}(t_1-t)=\left(\frac{2a}{1+\alpha t}-b\right)\frac{10334}{1{\cdot}293}(p_1-p).$$

Now, by the Mechanical Theory of Heat, the factor of t_1-t is equal to $424\times c$, where c is the specific heat for constant pressure; hence when $a=0{\cdot}002812$ and $b=0{\cdot}001976$ for air, and $c=0{\cdot}2377$, the last equation becomes, when $t=17°$,

$$424\times0{\cdot}2377\,(t_1-t)=\frac{10334}{1{\cdot}293}\times0{\cdot}00332\,(p_1-p).$$

If p_1 and p are expressed in kilograms per square metre, and if $p_0=10333$, this equation becomes

$$t_1-t=0{\cdot}265\,\frac{p_1-p}{p_0};$$

or, if p_1 and p remain expressed in atmospheres,

$$t_1-t=0{\cdot}265\,(p_1-p).$$

This equation, obtained for the first time, so far as I know, from theoretical considerations, is confirmed by experiment in the most striking manner. Thus for the factor whose approximate value we made 0·265, Joule and Thomson find the following values at temperatures not far from 17°:—

0·2502, 0·2637, 0·2429, 0·2881, 0·2606, 0·2531, 0·2565.

This factor must be smaller at higher temperatures. For 90° we should find it $=0{\cdot}18$. Joule and Thomson got 0·206 at this temperature; but the pressures at which their experiments were made were higher than those for which our equation is sufficiently exact.

In general the following equation holds for various gases, when the pressure is not too high,

$$424c(t_1-t)=\frac{10334}{1{\cdot}293d_0}\left\{\frac{2a}{1+\alpha t}-b\right\}\frac{p_1-p}{p_0}.$$

For carbonic acid, for which $a=0{\cdot}00874$, $b=0{\cdot}0023$, $d_0=1{\cdot}525$, and $c_{18}=0{\cdot}192$, we get for about 18° the equation

$$t_1-t=0{\cdot}9\frac{p_1-p}{p_0}.$$

At this temperature Joule and Thomson found a greater value for the factor, viz. 1·15. They did not, however, let the carbonic acid flow into an atmosphere of carbonic acid, but into a tube in communication with the atmospheric air. But I know no sufficient reasons to account for the great difference. At 91°·5 they found 0·703, while our formula requires 0·64. It is interesting to investigate whether in the original researches of Joule such a great amount of cooling was to be expected as could be observed calorimetrically. Joule filled a copper vessel of about 2·36 litres capacity with air at a pressure of 22 atmospheres. The temperature was about 15°, and the weight of air was thus about 0·064 kg. By opening a tap, leading into a similar vessel, the air was allowed to double its volume; under the condition of doing no external work. Therefore the cooling which resulted must be altogether ascribed to the gain of internal potential energy. By what has preceded we can calculate this gain thus,

$$\int_{v_1}^{v} ap_0\frac{v_0^2}{v^2}\,dv = ap_0v_0^2\left(\frac{1}{v_1}-\frac{1}{v}\right),$$

where v_0 denotes the volume of one kilogramme of air under one atmosphere pressure, and $v=2v_1$, v_1 being the initial volume. Since v is very nearly

$$=\tfrac{1}{11}v_0(1+\alpha t),$$

the amount of potential energy generated is

$$\frac{11ap_0v_0}{1+\alpha t} = \frac{11 \times 0{\cdot}002812 \times 10334}{1{\cdot}293 \times 1{\cdot}055} = 234 \text{ kilogram-metres.}$$

Thus the whole potential energy generated in the experiment was about 15 kilogram-metres, or the heat absorbed was 0·035 calorie.

The calorimeter contained about 8 kg. of water; and if we suppose that the above number of calories were taken from the water alone, the fall of temperature could not amount to more than 0°·0045, and this number must be considerably diminished if the water-equivalent of the calorimeter is taken into account. Now Joule gives $\frac{1}{200}$ of a degree Fahrenheit, or about 0°·003 Cel., as the smallest variation of temperature observable with his thermometer; so that, notwithstanding the great accuracy of his observations, it is not surprising that the above variation escaped him. If he had experimented on carbonic acid, probably he would have been able to observe the cooling.

It is easily seen that, *cæteris paribus*, the cooling effected in different gases is proportional to the values of a appropriate to them. The product p_0v_0 is inversely proportional to the density for different gases; but since for a vessel of given volume the weight of the contained gas is proportional to the density, these influences cancel. For carbonic acid the calorimeter would be cooled by at least 0°·01 C.

On the whole it follows that the proposition enunciated by Joule in 1845 ("On the Changes of Temperature produced by the Rarefaction and Condensation of Air," Phil. Mag. [3], May 1845, and 'Collected Papers,' vol. i. p. 182), is not rigidly correct: this proposition stated that "no change of temperature occurs when air is allowed to expand in such a manner as not to develop mechanical power."

The merit of Joule's discovery is not in any way diminished by this. He himself showed experimentally shortly afterwards, as we observed above, that his proposition was not perfectly accurate. It may even be regarded as a fortunate circumstance that Joule at first found no cooling. Perhaps the prophets of the "Caloric" school would have been less easily converted to a more correct view, if to the cooling of a gas when it does external work there could not have been opposed an absolute non-cooling when it does no external work.

Although the absolute statement was of great value at the time it was enunciated, we must regret that so little notice was taken of the correction supplied later on by Joule himself. There are still people who talk of perfect or ideal gases, and insist on treating the gases and vapours of nature as if they subscribed to the properties arbitrarily assigned to them. The misfortune of this treatment lies in the fact that the questions proposed and answered by those who adopt it have no reference to the facts of nature, but only to the arbitrary assumptions which gave rise to the questions. It is the boast of Thermodynamics that its laws do not rest on any assumptions as to the structure of matter, and consequently embody truths which are in so far unassailable. If, however, we are prevented from making more searching investigations into the nature of bodies through fear of leaving the region of invulnerable truths, then it is clear that by so doing we wantonly cut ourselves off from one of the most promising paths to the hidden secrets of nature.

To return to the consideration of an experiment like that made by Joule on the cooling of gases by expansion, we see that the cooling is so small that it can hardly be detected by calorimetrical experiments, though it may be rendered sensible by other methods. The gas, when it receives no heat from without, becomes cooled to a degree which is far from being negligible. In Joule's experiment, as we saw, the cooling was equivalent to 0·035 calorie. If this quantity of heat were taken from the air itself, the cooling would amount to $\frac{0{\cdot}035}{0{\cdot}064 \times 0{\cdot}1683}$, or about 3° C.

In general the number of degrees of cooling is given by

$$c_1\delta_1 = \mathrm{A}ap_0v_0\left(\frac{v_0}{v_1} \quad \frac{v_0}{v}\right).$$

Here δ_1 denotes the number of degrees, c_1 the specific heat for constant volume, A the heat-equivalent of the unit of work, while the remaining symbols keep their former meaning. If we compare this number of degrees with the cooling in

Joule and Thomson's arrangement of the experiment, given approximately by the equation

$$c\delta = \mathrm{A}p_0v_0\left(\frac{v_0}{v_1} - \frac{v_0}{v}\right)(2a-b),$$

where c denotes the specific heat for constant pressure, we see that when v and v_1 are the same in the two cases,

$$\frac{c_1\delta_1}{c\delta} = \frac{a}{2a-b},$$

or

$$\frac{\delta_1}{\delta} = \frac{a}{2a-b} \cdot \frac{c}{c_1}.$$

For air, therefore, δ_1 is somewhat greater than δ; whereas for carbonic acid δ_1 is less than δ.

Hitherto we have taken the specific heat for constant pressure to be given by

$$c = c_1 + \mathrm{A}p_0v_0(1+a)(1-b)\alpha.$$

The value as thus defined is not, however, quite accurate, as will appear from what follows.

The heat requisite to raise the temperature of a gas under constant external pressure consists of three parts :—First, the heat required to increase the kinetic energy ; secondly, the heat required to produce the new potential energy due to the external pressure having been overcome ; and thirdly, the heat requisite to increase the internal potential energy. The first part we call c_1dt, the second $\mathrm{A}pdv$, and the third $\mathrm{A}ap_0\frac{v_0^2}{v^2}\,dv$.

Therefore

$$cdt = c_1dt + \mathrm{A}\left\{p + ap_0\frac{v_0^2}{v^2}\right\}dv.$$

If p is constant, then

$$\frac{dv}{dt} = \frac{p_0v_0(1+a)(1-b)\alpha}{\left(p+ap_0\frac{v_0^2}{v^2}\right) - 2ap_0\frac{v_0^2}{v^2} \cdot \frac{v-bv_0}{v}};$$

therefore, approximately,

$$\left(p+ap_0\frac{v_0^2}{v^2}\right)\frac{dv}{dt} = p_0v_0(1+a)(1-b)\alpha\left(1+a\frac{p_0}{p}\frac{v_0^2}{v^2}\right)^2,$$

or

$$c-c_1 = A\alpha p_0 v_0 (1+a)(1-b)\left(1+a\frac{p_0}{p}\frac{v_0^2}{v^2}\right)^2.$$

If the constant pressure is the usual pressure of the atmosphere p_0, and if we put

$$v = v_0(1+\alpha_v t),$$

then

$$c-c_1 = A\alpha p_0 v_0 (1+a)(1-b)\left\{1+\frac{a}{(1+\alpha_v t)^2}\right\}^2.$$

Since we took the kinetic energy of the motion as our measure of temperature, c_1 is constant, provided the molecules are completely invariable. If c_1 is not constant, then

$$\frac{\int c\,dt}{t} = \frac{\int c_1 dt}{t} + A p_0 v_0 \alpha (1+a)(1-b)\left\{1+\frac{2a}{1+\alpha_v t}\right\}.$$

The quantity

$$p_0 v_0 (1+a)(1-b),$$

which we met before, is the limiting value of the product of the volume and pressure of 1 kg. of gas at 0°, which is continually rarefied. This appears from our equation

$$pv = (1+a)(1-b)p_0 v_0 - a p_0 \frac{v_0^2}{v} + b v_0 p + ab\frac{p_0 v_0^3}{v^2},$$

when $v=\infty$ and $p=0$.

If we examine the ratio of an element of the internal work to an element of the external work in the expansion of the gas, we get the expression

$$\frac{a\dfrac{p_0 v_0^2}{v^2}}{p},$$

which may be written

$$\frac{a}{(1+\alpha_v t)^2}\cdot\frac{v_0'}{v_0},$$

where v_0' denotes the volume at 0° under pressure p, and α_v denotes the coefficient of expansion.

If the pressure remains constant during the expansion, then v_0' does not alter for the different ratios of the elementary quantities of work, but on the contrary t alters. In order to find the mean value of the ratio between 0° and $t°$, we must find the mean value of $\frac{1}{(1+\alpha t)^2}$. This mean value is $\frac{1}{1+\alpha_v t}$ approximately. Consequently the ratio of the internal to the external work is

$$\frac{a}{1+\alpha_v t} \cdot \frac{v_0'}{v_0}.$$

If the expansion takes place under a pressure of one atmosphere, the ratio becomes

$$\frac{a}{1+\alpha_v t}.$$

For air between 0° and 100° this ratio is about ·002; for carbonic acid it is 0·0064. The ratio of the elementary quantities of work at 15° and under a pressure of one atmosphere is 0·0025 for air and 0·0079 for carbonic acid. These ratios were determined by Verdet (*Méc. de la Chaleur*, p. 102), from the observations of Joule and Thomson, to be 0·0020 and 0·0080 respectively.

The incomplete agreement between the values for air found theoretically and the values found by Verdet may well be ascribed to the many small quantities neglected by Verdet in his calculations. For carbonic acid, in particular, I have shown above that the cooling, as calculated by me, does not agree with that observed by Joule and Thomson. But it seems to me that the complete agreement for air warrants the correctness of the foregoing method of treatment.

The ratio of the two quantities of work is still small, even for carbonic acid, when the pressure is one atmosphere But, from the approximate equation for this ratio, viz.

$$V = \frac{a}{(1+\alpha_v t)^2} \cdot \frac{v_0'}{v_0},$$

it appears that at high pressures the ratio is nearly inversely proportional to the pressure.

Our definition of absolute temperature is not the only one that has been given. We defined it as proportional to the kinetic energy of the progressive motion of the molecules of a gas; from the equation of the isothermals we found that this amounted to making it proportional to the pressure of a given volume of gas, whatever the density might be—that, in other words, the absolute temperature according to our definition is given exactly by the readings of a gas-thermometer at constant volume, whatever be the nature of the gas.

Thomson (Phil. Trans. 1854, p. 351) gives another definition of absolute temperature. He takes the reciprocal of Carnot's Function as the absolute temperature. This is equivalent to making the temperature of a body proportional to the quantity of heat given up or received when it expands or contracts at constant temperature by a reversible process. Although Thomson considers that the temperature so determined is different from the temperature as shown by a gas-thermometer at constant volume, yet we can prove that the two definitions, apparently so different, yield a like result. Let dQ be the quantity of heat which a gas transforms into work, and which consequently it must receive from external sources, when the volume increases by dv, and the temperature according to our definition is constant; then, since there is both external as well as internal work to be done, we have

$$dQ = A\left\{p + ap_0\frac{v_0^2}{v^2}\right\}dv.$$

If the process is a reversible one, then p is the pressure of the gas. Now the equation of the isothermal shows that, instead of $p+ap_0\frac{v_0^2}{v^2}$, we may write

$$\frac{p_0v_0(1+a)(1-b)}{v-bv_0}(1+\alpha t);$$

therefore

$$dQ = Ap_0v_0(1+a)(1-b)(1+\alpha t)\frac{dv}{v-bv_0}.$$

Hence dQ is proportional to $1+\alpha t$ when the original volume and the change of volume is given; that is, dQ is proportional to the absolute temperature according to our definition. Hence, for a reversible cycle,

$$\int\frac{dQ}{1+\alpha t} = 0.$$

This result is even independent of the particular form found by us for the internal work.

We shall now apply our theory to the well-known problem of a gas expanding adiabatically. The required relation is given by the equation

$$c_1 dt + \mathrm{A}\left(p + ap_0\frac{v_0^{\,2}}{v^2}\right)dv = 0.$$

Substituting the value

$$p + ap_0\frac{v_0^{\,2}}{v^2} = \frac{(1+a)(1-b)\,p_0 v_0(1+\alpha t)}{v - bv_0},$$

we get

$$\frac{c_1\alpha dt}{1+\alpha t} + \mathrm{A}p_0 v_0 \alpha(1+a)\,(1-b)\,\frac{dv}{v-bv_0} = 0,$$

or, integrating,

$$c_1 \log\frac{1+\alpha t_1}{1+\alpha t_2} = -\mathrm{A}p_0 v_0 \alpha(1+a)\,(1-b)\log\frac{v_1 - bv_0}{v_2 - bv_0}.$$

Let c_2 denote the limiting value of c, the specific heat at constant pressure, when $v = \infty$; then

$$c_2 = c_1 + \mathrm{A}p_0 v_0 \alpha(1+a)\,(1-b)\,;$$

therefore

$$c_1 \log\frac{1+\alpha t_1}{1+\alpha t_2} = -\,(c_2 - c_1)\log\frac{v_1 - bv_0}{v_2 - bv_0},$$

or

$$\frac{1+\alpha t_1}{1+\alpha t_2} = \left(\frac{v_2 - bv_0}{v_1 - bv_0}\right)^{\frac{c_2}{c_1}-1}.$$

This equation may also be written

$$\left(\frac{v_2 - bv_0}{v_1 - bv_0}\right)^{\frac{c^2}{c^1}} = \frac{\dfrac{1+\alpha t_1}{v_1 - bv_0}}{\dfrac{1+\alpha t_2}{v_2 - bv_0}} = \frac{p_1 + ap_0\dfrac{v_0^{\,2}}{v_1^{\,2}}}{p_2 + ap_0\dfrac{v_0^{\,2}}{v_2^{\,2}}}.$$

Hence the equation of the adiabatic curve is

$$(v - bv_0)^{\frac{c_2}{c_1}}\left(p + ap_0\frac{v_0^{\,2}}{v^2}\right) = \text{constant}.$$

If b and a are zero, this becomes Poisson's formula.

Chapter XII.*

Corresponding Properties of the Normal Curves of various saturated Vapours and Liquids, and an indication of the Form of these Curves for Mixtures.

From the preceding considerations, it appears that each isothermal for a body below the critical temperature has two points which may be regarded as the limits up to which the body is able to fill the assigned space while remaining homogeneous. The locus of these points belonging to a series of isothermals depends on various circumstances—the nature of the walls and the form of the space, &c. Provisionally we may consider as the most important points those which correspond to the saturated vapour and to the liquid in such a condition that a continuous transition may be effected from one state to the other without change of pressure. These points lie at a height above the axis of abscissæ, which is the mean of the ordinates of the theoretical curve, as was shown by Maxwell in 1875 and by Clausius in 1879.

The origin of coordinates being as usual to the left, then, on the right-hand part of the locus, lies the series of points which give the volume and pressure of the saturated vapour (Pl. V. fig. 3). With higher temperatures the pressure increases and the volume diminishes. At a certain height the curve has a point of inflexion, and in the neighbourhood of the critical point the summit is reached.

At this point the curve in question joins the curve which gives the volume of the liquid at the pressure of the saturated vapour. This "water-line," as it is called, descends slowly at first, but rapidly becomes steep, as it corresponds to liquid volumes only slightly greater than the least possible volume. Under these circumstances the space enclosed between it and the axis of pressures becomes very narrow.

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* [The twelfth and thirteenth Chapters contain later papers by the Author, published under the above titles in the Transactions of the *K. Akad. van Wetensch.*, Amsterdam, 1880.—*Note by the German Translator.*]

The equation of this curve has not hitherto been discovered. I long thought it very probable that for bodies which are not subject to peculiar conditions, such as dissociation, and the molecules of which therefore may be supposed to move independently of each other, this curve must have the same equation for all bodies, but with different constants for different bodies. And these constants could only be those we denote by a and b.

Starting from the equation

$$\left(p+\frac{a}{v^2}\right)(v-b) = \mathrm{R}(1+\alpha t),$$

and using the law of Maxwell and Clausius mentioned above, I repeatedly tried to find the equation of the curve made up of the water- and steam-line. This curve I shall in future call, for shortness, the "Border-Curve."

This I effected for the first time after studying Gibb's Thermodynamic Surface. This surface is the locus of points whose coordinates are the volume, energy, and entropy. The curve here spoken of is given by the surface as the locus of points whose tangent planes touch the surface a second time. But I soon saw that the calculations were not simplified by using the surface, since, by introducing simplifications, we are merely led back to the same method of treatment as arises from the law of Maxwell and Clausius.

I was prevented from publishing my result, not only by the wearisome calculation and the complexity of the final equation, but also by the following considerations :—The equation given above holds only for volumes greater than $2b$. Now, if we employ the Maxwell-Clausius law, the result will hold only for a small portion of the curve considered, viz. that in the neighbourhood of the highest point. It is, however, just for pressures far removed from those corresponding to the highest point of the curve that the most accurate experiments have been made on saturated vapours. Thus data for purposes of comparison were not to hand.

Respecting the equation of the curve my view has remained the same. I have been able to make a calculation for the mutual comparison of the curves for different bodies. Though this equation holds only with certainty in the neighbourhood of the critical temperature, it may be applied with probability to the whole course of the curves in question.

From the equation

$$\left(p+\frac{a}{v^2}\right)(v-b) = \mathrm{R}(1+\alpha t), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

we get, for the critical point (see p. 420) :—

critical pressure . . . $p_1 = \frac{a}{27b^2}$,

critical volume . . . $v_1 = 3b$,

critical temperature . . $1+\alpha t_1 = \frac{8}{27}\frac{a}{b\mathrm{R}}$.

Now putting

$$p = \epsilon p_1, \quad v = nv_1, \quad 1+\alpha t = m(1+\alpha t_1),$$

(1) becomes

$$\left(\epsilon+\frac{3}{n^2}\right)(3n-1) = 8m. \quad . \quad . \quad . \quad . \quad (2)$$

Thus, if we express the pressure in terms of the critical pressure, the volume in terms of the critical volume, and the absolute temperature in terms of the absolute critical temperature, the isothermal for all bodies becomes the same.

This result, then, no longer contains any reference to the specific properties of various bodies, the "specific" has disappeared. I omit at first numerous consequences, and only call attention to the property that at the critical point the product pressure by volume must be always the same fraction of the product deduced from the laws of Boyle and Gay-Lussac.

The curve given by equation (2) I shall call the "Reduced Isothermal." If the Maxwell-Clausius law be applied to this curve, then of course for all bodies the same points of section will be found ; and we shall get a "Reduced Border-Curve," from which the border-curve for each body can easily be found.

By the Maxwell-Clausius law of the equality of areas, the following equation holds,

$$p(\gamma-v)=\int_v^\gamma p\,dv;$$

where γ denotes the volume of the saturated vapour, and v the liquid volume,

or
$$p(\gamma-v)=\mathrm{R}(1+\alpha t)\log\frac{\gamma-b}{v-b}+\frac{a}{\gamma}-\frac{a}{v}.$$

Again introducing

$$p=\epsilon p_1,\ 1+\alpha t=m(1+\alpha t_1),\ \gamma=n_3v_1, \text{ and } v=n_1v_1,$$

we get

$$\left(\epsilon+\frac{3}{n_1n_3}\right)(n_3-n_1)=\frac{8}{3}m\log\frac{3n_3-1}{3n_1-1}.$$

Joining to this the equations

$$\left(\epsilon+\frac{3}{n_1{}^2}\right)(3n_1-1)=8m$$

and

$$\left(\epsilon+\frac{3}{n_3{}^2}\right)(3n_3-1)=8m,$$

we get by elimination a relation between ϵ and m.

If we express this relation by

$$\epsilon=\phi(m),$$

then the form of this function is independent of the nature of the body, or, in other words, "If the absolute temperature is the same fraction of the absolute critical temperature for different bodies, then the pressure of the saturated vapours of these bodies is the same fraction of the critical pressure."

If n_1 and ϵ are eliminated we get a relation between m and n_3; and if m and n_1 are eliminated we get a relation between n_3 and ϵ. The equation

$$n=\psi(m)$$

must then have at least two roots for n, and the form of the function ψ must be the same for all bodies. Hence the second proposition: "If the absolute temperature of any two liquids is the same fraction of their respective critical temperatures, then the volume both of the liquids and of their saturated vapours is the same fraction of their critical volumes."

A similar proposition holds for the difference n_3-n_1; thus if $n_3=\psi_3(m)$ and $n_1=\psi_1(m)$, then

$$n_3-n_1=\psi_2(m).$$

In the same way we arrive at

$$n=\xi(\epsilon).$$

This result may be expressed geometrically thus :—"If the border-curves of bodies coincide at their highest points, they coincide altogether." Clausius (Wied. *Ann.* ix. p. 337, 1880) has made a change in equation (1) which leads to the following form

$$\left(p+\frac{a}{\mathrm{T}(v+\beta)^2}\right)(v-b)=\mathrm{RT}. \quad . \quad . \quad . \quad (4)$$

Without going more closely into the objections I have to this alteration, I will show that this form leads to just the same results as were obtained above.

Putting $v+\beta=v'$ we have

$$\left(p+\frac{a}{\mathrm{T}v'^2}\right)\left(v'-(b+\beta)\right)=\mathrm{RT}.$$

Again denoting the critical pressure, critical volume, and absolute critical temperature by p_1, v_1, T_1 respectively, then

$$p_1=\frac{a}{27\mathrm{T}_1(b+\beta)^2}, \quad v_1=3b+2\beta, \quad \mathrm{T}_1^{\,2}=\frac{8}{27}\,\frac{a}{(b+\beta)\mathrm{R}}.$$

Further, putting

$$p=\epsilon p_1, \quad \mathrm{T}=m\mathrm{T}_1, \quad v=n(v_1+\beta)-\beta,$$

then (4) becomes

$$\left(\epsilon+\frac{3}{mn^2}\right)(3n-1)=8m.$$

By using the Maxwell-Clausius law, we get

$$\left(\epsilon+\frac{3}{mn_1n_3}\right)(n_3-n_1)=\frac{8}{3}m\log\frac{3n_3-1}{3n\;-1}.$$

Having regard to

$$\left(\epsilon+\frac{3}{mn_3^{\,2}}\right)(3n_3-1)=8m,$$

and

$$\left(\epsilon+\frac{3}{mn_1^2}\right)(3n_1-1)=8m,$$

we again obtain the foregoing propositions $\epsilon=\phi'(m)$ with

$$n_3=\psi_3(m), \quad n_1=\psi_1(m), \quad n_3-n_1=\psi_2(m).$$

Finally, since

$$n_3-n_1=\frac{\gamma-v}{3(b+\beta)}=\psi_2(m),$$

we see as a result of Clausius' equation that the reduced border-curves for all bodies are similar, though not coincident, when the volume is expressed as a multiple of $b+\beta$, the pressure as a multiple of the critical pressure, and the temperature as a multiple of the critical temperature.

Clausius considers his equation to be true for all volumes, and therefore even for those parts of the border-curve which are far from the highest point. Yet observations do not afford a confirmation of the equation given by him.

We have already seen that two different laws of the isothermal yield identical results so far as the border-curve is concerned. It may therefore be reasonably expected that these two laws will lead to like results for saturated vapours in those cases where the value of b is considered to vary—it being understood that the variations of the states of the bodies are corresponding variations. According to my method of treatment we only deal with cases represented by the statement that the volume must be taken as greater than $2b$; and consequently our expectation will only apply to such cases.

There is ample material at hand to verify whether, in the equation

$$\epsilon=\phi(m),$$

ϕ has the same form for all bodies. For this purpose we may consider all bodies whose critical pressure and critical temperature are known, and for which observations of the vapour-tension are to hand. The list will include carbonic acid, ether, hydrochloric acid, ethylene, carbon bisulphide, sulphurous acid, and others. I have ventured to exclude alcohol, since the data for the critical point differ so much that the observers evidently really experimented with different bodies. Thus Cagniard de la Tour gives $p_1=119$, $T_1=532°$, while Sajotschewsky gives (*Beibl.* iii. p. 741, 1879) $p_1=62·1$, and $T_1=507°·3$. The inconsistencies may be due to the alcohol used having been contaminated with water to an extent which differed in the different experiments.

In the case of other bodies for which observations afford better results, it must not be forgotten that the critical pressure more particularly is not known with any great accuracy. This is due not only to the fact that the smallest admixture with foreign substances causes a great variation of pressure at the critical point; but also to the fact that the pressure (since it was determined by the application of Boyle's law to the change of volume of some permanent gas used manometrically) cannot be considered as accurately known.

Consequently complete agreement can scarcely be expected in the following tables. Yet the agreement is always so good, that the law laid down must be regarded, if not as absolutely correct, yet as approximately determining the form of the vapour-line.

As a beginning I will make a comparison between ether and sulphur dioxide, two bodies of very different constitution. The critical pressures are also widely different. The necessary data are taken from the observations of Sajotschewsky. These give the vapour-tension only for intervals of 10°, and some of the values are fixed by interpolation :—

Sulphur Dioxide.	Ether.
$p_1=78·9$, $T_1=428°·4$.	$p_1=36·9$, $T_1=463°$.

As an example Sajotschewsky gives for sulphur dioxide $t=150°$ when $p=71·45$.

Corresponding to the same value of ϵ, for ether the pressure is 33·45, and from the table we find 183°·3 as the corresponding temperature. Therefore

$$m \text{ for sulphur dioxide} = \frac{273+150}{428·4} = 0·987,$$

$$m \text{ for ether} = \frac{273+183·3}{463} = 0·986.$$

p.		$m.10^3$.	
SO_2.	Ether.	SO_2.	Ether.
60	28·4	964	963
49·97	23·4	941	940
41·56	19·4	918	918
33·95	15·9	894	895
27·82	13·0	871	872
22·47	10·5	848	849
18·09	8·46	825	828
14·31	6·69	801	807
11·09	5·18	777	784
8·43	3·94	754	762

A more extended comparison is not possible, since Sajotschewsky's observations go no further. If we calculate at what temperature ether has the pressure 3·94 atmospheres we should find it to be 76°, the observed temperature is about 79°.

If we consider that in all the observations quoted the pressure, so far from being observed directly, was calculated from the change of volume of some gas, we shall be inclined to admit that the numbers in the table afford a very good—if not a perfect—verification of the law.

The best test, however, is applied by calculating the value of m from the values of ϵ for each body. This is shown for some bodies in the following table. The values of ϵ and m are multiplied by 10^3.

(1) *Ether* ($p_1=36{\cdot}9$; $T_1=463°$). [*Note.*—ϵ_1 is the value according to Regnault, ϵ_2 according to Sajotschewsky.]

Regnault.	Sajotschewsky.		Regnault.	Sajotschewsky.	
ϵ_1.	ϵ_2.	*m.*	ϵ_1.	ϵ_2.	*m.*
	1	1	139	139	784
	865	978	108	108	763
	726	957	82	82	741
	605	935	61·5	61·5	719
	505	913	45·1		697
	418	892	32·3		676
	344	870	22·6		654
275	282	848	15·4		633
222	226	827	10·2		611
177	178	806	6·6		590

(2) *Sulphurous Acid; Monochlorethane*, $p_1=52{\cdot}6$, $T=455°{\cdot}6$ (according to Sajotschewsky); *Carbonic Acid*, $p_1=72$, $T_1=303°{\cdot}9$ (according to Andrews).

Sulphurous Acid.		Monochlorethane.		Carbonic Acid.			
ε(1)	*m.*	ε(2).	*m.*	ε.	*m.*	ε.	*m.*
104·7	754	1	1	1	1	269	832
77·8	731	800	972	822(3)	969	510(5)	895
57·2	708	681	950	669	941	421	876
41·0	684	574	928	893(4)	981	367	858
28·7	661	480	906	795	964	312	840
18·4	637	398	884	622	931	266	821
12·7	614	330	862	479	898	223	803
8·0	591	282	840	362	865	185	786

[*Note.*—(1) is according to Regnault; (2) Sajotschewsky; (3) to (4) Andrews; from (4) to (5) Regnault; from (5) to the end Faraday.]

The numbers of the individual observers differ so considerably that the law can be only approximately tested by means of them; for example, according to Regnault's values for carbonic acid, when $\epsilon=0{\cdot}269$, then $m=0{\cdot}832$; while, according to Faraday, for nearly the same value of ϵ, $m=0{\cdot}821$.

That the law is of practical importance appears from its enabling us to calculate the temperature at which a vapour has a given pressure.

For example, let us calculate the boiling-point of carbonic acid under the pressure of one atmosphere, supposing the observations for ether-vapour to be given. We must first find what value of p in the case of ether gives a value of ϵ equal to the value of ϵ for carbonic acid when $p=1$; and for this we get 384 mm. The corresponding temperature is about $16^\circ{\cdot}9$, and therefore $m=0{\cdot}625$. Hence the absolute temperature is about $0{\cdot}625\times303{\cdot}9$, or $t=-83^\circ$. Faraday observed $p=1{\cdot}2$ when $t=-79^\circ$. Since further $p=1{\cdot}8$ when $t=-73^\circ{\cdot}3$, it follows that by observation we get $t=-81^\circ$ for $p=1$.

The formula can also be used to calculate the critical pressure and volume, when we are in possession of observations for the vapour-pressures. Thus the critical temperature of water is only approximately known, and as to the critical pressure we only know that it must be pretty high. If we take the critical temperature to be $410+273$, then we must compare the vapour-pressures for temperatures which are given fractions of 683°, with the vapour-pressures for ether, say at temperatures which are the same fractions of 463°.

If the critical temperature of water has been rightly chosen, then the ratio of the corresponding vapour-pressures of the two bodies must be constant, and this ratio must be that of the critical pressures.

One set of corresponding temperatures are:—

for Ether	$t=0$	10	20	30	40	50
for Water	$t=128$	142·7	157·4	172·1	186·8	201·5

and the vapour-pressures in millimetres:—

for Ether	184	286	432	634	907	1264
for Water	1920	2917	4330	6250	8800	12050.

Hence follow the ratios

10·3 10·2 10 9·8 9·6.

These do not remain constant, but diminish continually, and, probably, the critical temperature of water has been taken too high. If instead we take this to be 390°, we get the ratios

7·63 7·6 7·5 7·52 7·55,

and for 7·55 as the value of the ratio, the critical pressure of water $=7{\cdot}55 \times 36{\cdot}9=278$ atmospheres. This number, however, can only be regarded as an indication of the approximate value of the critical pressure, since we are not quite certain whether our law is accurate for points considerably removed from the highest point of the border-curve.

Let us now examine how far the equation

$$n_3-n_1=\psi_2(m)$$

is confirmed by observation. With this view let us write it in another form, viz.

$$\frac{\mathrm{V}-v}{v_1}=\psi_2(m)\,;$$

where V denotes the vapour-volume, and v the liquid-volume. If we take a kilogram as unit of weight, then $\mathrm{V}-v$ is usually denoted by u. The value of v_1 is $3b$. The unit of volume is the volume of the body at 0° under a pressure of one atmosphere. Let this volume be σ, then

$$\frac{u}{3b\sigma}=\psi_2(m).$$

Now σ is inversely proportional to the molecular weight μ, and therefore

$$\frac{u\mu}{b}=f(m)=\mathrm{F}(\epsilon).$$

Expressed in words this is :—

"The difference between the vapour specific volume and liquid specific volume, multiplied by the molecular weight, and divided by the volume of the molecules, is the same for all bodies at pressures which are the same fraction of the critical pressures."

The last form is best adapted for use, while the first gives the law in a simpler form.

Extremely few observations have been made in the neighbourhood of the highest point of the border-curve, and we must therefore be satisfied with a comparison of other parts of the curve. Let us leave b out of account provisionally so as not to be obliged to make use of a quantity not yet accurately determined. Thus we examine whether the values of u for two bodies always have the same ratio. And first for ether and steam, for which last 390° is taken as the critical temperature. The following table gives the results obtained ; the column t contains the temperatures for ether which correspond to the temperatures t_1 for steam; u and u_1 are the values for these temperatures borrowed from Zeuner's tables; and the last column contains the ratio of u to u_1.

t.	t_1.	u.	u_1.	$\frac{u}{u_1}$.
0	118	1·272	0·924	1·37
10	$132\frac{1}{3}$	0·839	0·611	1·37
20	$146\frac{2}{3}$	0·571	0·418	1·36
30	161	0·398	0·293	1·36
40	$175\frac{1}{3}$	0·285	0·210	1·36
50	$189\frac{2}{3}$	0·209	0·155	1·35
60	204	0·156	—	—

Now since

$$\frac{u\mu}{b} = \frac{u_1\mu}{b'},$$

we can calculate b from the value of the ratio. We have $\mu=18$, $\mu'=74$, therefore $b=\frac{b'}{5{\cdot}5}$. Presently we shall determine b' to be 0·00575 from the observations of Sajotschewsky ; hence for water $b=0{\cdot}00105$.

We can show the correctness of the value for b by using it in the equation $p_1=\frac{a}{27b^2}$ to calculate the critical pressure of steam. Since $\frac{a}{b}$ is found from the critical temperature to be 8·2, we get $p_1 = 289$, a number which does not differ so very much from the number found before, viz. 278 atmospheres. A test of the truth of the formula $\frac{u\mu}{b} = f(m)$ may also be made by considering those bodies for which b can be determined in some other way. We first give a set of observed critical temperatures and pressures, and the values of b thence derived. The names of the observers are abbreviated, thus: A = Andrews, S = Sajotschewsky, H = Hannay, C = Cagniard, W = van der Waals, An = Ansdell, J = Janssen.

	p_1.	t_1.	$b \,.\, 10^5$.
Carbonic Acid (A)	73	30·9	200
Ether (S)	36·9	190	575
Carbon Bisulphide (S)	74·7	271·8	334
Sulphurous Acid (S)	78·9	155·4	249
Alcohol (S)	62·1	234·3	374
„ (H)	65	234·6	356
„ (C)	119	256	203
Monochlorethane (S)	52·6	182·5	397
Benzol (S)	49·5	280·6	513
Acetone (S)	52·2	232·8	444
„ (S)	60	237·5	390
Chloroform (S)	54·9	260	444
Ethylene (W)	58	9·2	223
Hydrochloric Acid (An)	86	51·25	173
Acetylene (An)	68	37	209
Carbon Tetrachloride (H)	58·1	277·9	436
Carbon Bisulphide (H)	77·9	273	321
Nitrous Oxide (J)	73·07	36·4	194

In constructing the following table we have borrowed from Zeuner's tables a set of pressures and the corresponding values of u; the third and fourth lines contain μ, the molecular weight, and b; the fifth line gives the quotient $\frac{u\mu}{b}$ denoted by x; the three last lines are as denoted by the letters, and refer to another series of experiments.

	Ether.	Alcohol.	Acetone.	Chloroform.	Carbon Tetrachloride.
p	4953	8325	6982	7400	7826
u	0·056	0·058	0·056	0·027	?
μ	74	46	58	119·5	154
$b.10^5$	575	374	444	444	436
x	721	714	731	727	
p	2476	4162	3491	3700	3913
u	0·113	0·118	0·113	0·053	0·036
x	1455	1451	1476	1430	1300

The law is also confirmed for other pressures similarly treated. We see, however, that there is a deviation in the cases of carbon tetrachloride and carbon bisulphide; nevertheless, if we consider the number of experimental determinations on which these quantities depend, it is evident they ought not to be treated as affording any reason for supposing that the equations are merely approximate.

If we start with Clausius' equation of the isothermals there will be little to alter in the foregoing. We must have $\frac{u\mu}{b+\beta}$ the same for all bodies for equal reduced pressures of temperatures. The quantity $b+\beta$ is calculated from the data of the critical point in the same manner as b was calculated, only with this difference, that our b denotes four times the volume of the molecules, while with Clausius the quantity so calculated must be first diminished by the unknown β in order to give a measure of the same quantity.

Some further properties of the different border-curves may be deduced. For instance, supposing that there is a maximum value of pu for any single gas or vapour, then the product pu for all gases and vapours must have a maximum value at *equal* reduced temperatures. But, having regard to the uncertainty in the values of pu, we can only expect an approximate confirmation of this. In the case of four bodies, Zeuner's tables furnish us with this maximum value; for ether at a certain reduced temperature it is about 0·8, and nearly the same maximum value is found for acetone, carbon tetrachloride, and carbon bisulphide, viz. 0·8, 0·73, and 0·74 respectively.

If our equations are right, a relation may be found between the latent heat of vaporization of different bodies.

Thus in the usual equation for latent heat

$$\frac{dp}{dT} = \frac{r}{ATu};$$

putting for p, T, and u the values ϵp_1, mT_1, and $\frac{f(m)b}{\mu}$ respectively, we get

$$\frac{d\epsilon}{dm} = \frac{8 \times 273}{A} \cdot \frac{r\mu}{T_1} \cdot \frac{1}{mf(m)}\text{*}.$$

Now since for the same value of m, that is at the same reduced temperature, $\frac{d\epsilon}{dm}$ is the same for all bodies, we have

$$\frac{r\mu}{T_1} = F(m),$$

and this is the same for all bodies at the same reduced temperature.

This relation calls to mind Despretz's proposition. The last equation may be written

$$\frac{r}{up_1} = \psi(m).$$

According to Despretz, $\frac{r}{u}$ is the same for all bodies at the temperatures at which the vapour-pressures are equal. By our equation $\frac{r}{u}$ is proportional to the critical pressure, when the reduced temperatures of the bodies are equal. We will give some numbers to show how far the formula

$$\frac{r\mu}{T_1} = F(m) = \phi(\epsilon)$$

agrees with observation.

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* [This equation is slightly altered from the one given in the German edition. We have corrected a mistake of $\phi(m)$ for $f(m)$ and u for μ. But even so we are unable to arrive at the same result. We think the equation should be

$$\frac{d\epsilon}{dm} = \frac{r\mu}{Abp_1mf(m)},$$

which destroys the argument.—Note by the English Translators.]

The following table gives, for several bodies, the value of r at the pressure p expressed in atmospheres; the line marked y contains the quotients $\frac{r\mu}{T_1}$.

	Water.	Ether.	Acetone.	Chloroform.	Carbon Tetrachloride.	Carbon Bisulphide.
p	7·5	1	1·41	1·49	1·57	2·03
r	489	90	126·5	60	45	82
y	1·35	1·31	1·44	1·35	1·34	1·15

Judging by these numbers, the laws enunciated seem to hold only approximately for points far removed from the end of the steam- and water-lines. Observations in the neighbourhood of this limit are not to hand. The empirical formulæ for the latent heat at high temperatures are certainly not valid. There is no single one of them which gives $r=0$ for the critical temperature, even approximately.

It is to be remarked that the law for r requires it to depend on m in a similar manner for all bodies. Now this is not expressed in the empirical formulæ; nor, after what has been said, ought we to expect it.

The vapour-pressures of various bodies have lately been repeatedly compared, with a view to obtaining a method of deducing the properties of one vapour from those of another. In particular Winkelmann (Wied. *Ann.* ix. p. 208, 1880) has given an equation which holds for various vapours; the equation is of quite the same form as ours, only with constants of different value. In his equation two of the quantities p, v, T do not occur, but the three quantities t, p, and the density or v take their place. If we calculate the quantity which Winkelmann denotes by $\frac{d_n}{d}$ from the equations for the critical temperatures of different bodies, we do not find $\frac{8}{3}$, but a much smaller number. This is proof enough that Winkelmann's law can correspond only approximately to those parts of the vapour-line which are sufficiently removed from its culminating point.

Similarly the law given by Dühring (Wied. *Ann.* xi. p. 163, 1880) and by Mondésir (*Beibl.* v. p. 52, 1881) can have no all-embracing validity, since in it no regard is paid to that pervading inequality of the critical pressure which really exists. This law, however, becomes identical with mine, when in its expression we substitute equal reduced pressure for equal pressure. For when the reduced pressures are equal we have for the relation between t_1 and t_2 the linear equation

$$\frac{1+\alpha t_1}{T_1}=\frac{1+\alpha t_2}{T_2},$$

which, when expressed in the form

$$t_1=r+qt_2,$$

gives Dühring's law.

If two bodies should have the same critical pressure, then my law, *as far as they are concerned*, would be identical with Dühring's. This is approximately the case for carbonic acid and nitrous oxide. The critical temperature of carbonic acid is 303°·9, of nitrous oxide 309°·4; and consequently, if t_1 is the temperature of carbonic acid, t_2 that of nitrous oxide, at which the pressures are equal,

$$273+t_2=1{\cdot}0181\ (273+t_1),$$

or

$$t_2-t_1\ =4{\cdot}9+0{\cdot}0181t_1.$$

The term $0{\cdot}0181t_1$ becomes considerable only when t_1 is very different from 0°, and hence it follows that for these two bodies a difference of from 4° to 5° exists between the temperatures at which the pressures are equal. According to Faraday's observations we have

p.	t_1.	t_2.
73	+30·4	+36·4
30·7	− 6·7	− 1·6
26·8	−12·2	− 6·7
19·4	−23·3	−17·9
5·3	−56·7	−51·5
2·8	−67·8	−64·3

For lower temperatures the law would cease to be valid, even supposing we could still rely on the accuracy of the observations.

That Dühring's law should give values corresponding to the observations, at least for a part of the border-curve, is to be expected; but this only follows from the particular relation between p and t for each body, which is assumed by him.

The relation has not, however, been proved for other parts of the curve, and ceases to be valid towards the highest point of it.

In general therefore we must reject, as not possessing any rational signification, all relations from which are deduced properties for equal pressures or equal temperatures. For since the critical pressures are usually different there can never exist a general relation between the properties of different bodies at the same pressure. This will become obvious if we consider two bodies; one of which alone is at its critical pressure. In this case it is clear that the bodies are under such different conditions that their pressure relations cease to be comparable. From this it follows that most of the relations generally expressed are deprived of much of their signification.

There is one law, however, which in the light of our researches appears to be well founded—this is Kopp's law for the determination of molecular volumes. As the matter appears to me this law really consists of two general statements, each of which is independently based on a distinct hypothesis. The first assumption is that a relative measure of the magnitude of the molecules is obtained by multiplying the space occupied by a gram of the liquid by the molecular weight. Evidently this is true if, first, all the molecules are in contact, or if, secondly, the whole volume is an invariable multiple of the volume occupied by the molecules. Kopp's law really rests on this last hypothesis, but hitherto no proof of it has been given, unless indeed the second part of the law, that which enables the volume of the molecules to be calculated by attributing fixed relative sizes to the atoms, be considered in a certain sense as an indirect proof.

From the equation

$$n=\psi(m),$$

where $n=\frac{v\mu}{b}$, and b denotes four times the volume of the molecules, we immediately get the equation

$$\frac{v\mu}{b}=\psi(m)$$

as the expression of Kopp's law ; only the volume v is not to be taken for temperatures of equal vapour-pressure, but for temperatures of equal reduced vapour-pressure. Kopp's law is usually applied only at a pressure of one atmosphere, and therefore the deviation will be insignificant. Nevertheless preference ought to be given to the expression of b by means of the critical point, were it not that the critical pressure is considerably altered by the smallest admixture with a foreign body.

The foregoing results relate to bodies which can be obtained in a state of nearly complete purity. The curve giving the limit within which the space occupied by a body can be homogeneously filled may be called the Normal Curve. In many respects, however, the border-curve may deviate considerably from its normal form, especially if we are dealing with a mixture and not with a homogeneous body in which all the molecules are of equal size. Although we have no observations which place the existence of such a curve beyond doubt, yet in my opinion there are theoretical and experimental facts enough to make its existence highly probable. Some indications as to the direction of the deviation of the border-curve from the normal form have already shown themselves; a closer investigation may be postponed for further enquiry.

Hitherto in the treatment of a mixture of two or more bodies, the behaviour for each ingredient has been assumed to be almost altogether independent of the others. This method of treatment finds its most definite expression in Dalton's law referring to mixtures of gases. The ingredients are here considered separately, but according to my view more satisfactory results would be arrived at by considering the mixture as a whole. In favour of this point of view it may be said first that a mixture, as well as a simple body, has a critical temperature, above which it is possible for it, while remaining homogeneous, to assume any volume. This temperature naturally depends on the critical temperatures of the ingredients of the mixture, and on the relative quantities of these ingredients, but is not necessarily the same as that belonging to any one of them*.

There are some considerations which make it appear probable that the critical temperature of a mixture may even lie beyond the critical temperatures of its ingredients.

Above this temperature the mixture behaves as if it were homogeneous. The form of the isothermal appears either to agree completely with that of a simple body, or at least to follow it in its principal features. Observations on the compressibility of gases, and on the influence of temperature, have been carried out principally on air, which is a mixture ; and they show so much agreement with the behaviour of simple bodies, that they tend to obscure this important difference.

For each kind of compound there are certain values of a and b, which are of course related both to the corresponding values of these quantities for the components, and to the nature of the compound. Then the critical point must also depend on a and b in the same way as it does in the case of a simple body. And just as for a simple body below the critical temperature, a part of the isothermal cannot be realized, on account of the instability of the equilibrium, so is this the case for mixtures. To the right- and left-hand of this part of the isothermal, the body can again fill space homogeneously.

If these considerations are valid, then a mixture must behave as if it were homogeneous, whether it is made to occupy a very great or a very small space. For great volumes this is universally acknowledged, and at every temperature a mixture of two gases or vapours can uniformly occupy a great space. At first I thought that there were no experiments for very small volumes, and I experimented with Cailletet's pump on a mixture of air and carbonic acid, and afterwards on other mixtures in chosen proportions.

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* [The results of Cailletet and Hautefeuille lend some colour to this method of treatment. C. R. xcii. p. 901, 1881.—*Note by the German Translator.*]

A mixture of 9 volumes of carbonic acid and one volume of air had the critical temperature 25° and the critical pressure 77·5 atmospheres. At 23°·5 and $p=73$ a separation into two parts took place. When the volume was further diminished, the pressure increased, and at 95 atmospheres the mixture again became homogeneous. The same changes occurred for the values 20°·4, 72 atmospheres and 103 atmospheres; the mixture was homogeneous at 19°·2 and 106 atm.; also at 2° and 145 atm.

For a mixture of 7 volumes carbonic acid and 3 volumes hydrochloric acid the following were the results:—

Critical temperature 31°·6; critical pressure 90 atm.

	Pressure at which Condensation occurs.	Pressure at which Homogeneity is restored.
$t=22·5$	$p=69$	115
$t=0$	$p=39$	150

I found afterwards that these phenomena had been observed by Cailletet (*Beibl.* iv. p. 322, 1880).

He found, for a mixture of 5 volumes carbonic acid and 1 volume air, that homogeneity occurred again at

	$t=5°·5$	10	13	18	19
and					
	$p=132$	124	120	113	110

In addition, the experiments of Hannay on the solubility of solid bodies in (liquified ?) gases may be used to confirm the foregoing results (*Beibl.* iv. p. 771, 1880; compare also Kundt, Wied. *Ann.* xii. p. 538, 1881).

At first sight it appears strange that with decreasing temperature the pressure at which homogeneity recurs increases. But an explanation of this can easily be found.

Imagine a mixture of carbonic acid and air below the critical temperature to be compressed. At first the volume is large, and the space is uniformly filled; then a volume is reached at which a separation into two parts, of greater and less density, takes place. In consequence of this separation, the constitution of the two parts is now no longer the same. Thus the part whose density is greater will chiefly consist of carbonic acid, mixed with a little air; while the part whose density is less will consist chiefly of air. The constitution also alters with diminution of volume. The carbonic acid gets to contain more air, and the air more carbonic acid. Finally, at higher pressures the constitution of the two parts is again the same, and the mass regains its homogeneity.

The limiting points do not lie at the same height on the isothermal: the point corresponding to the smaller volume is at a greater height than the other. The theoretical isothermal is cut here, not by a straight line parallel to the volume-axis, but by a curved line whose exact form is at present scarcely capable of determination. It will depend on the nature of the components and on their relative quantity; but this much follows from the foregoing, that the left-hand part of the border-curve is bent upwards.

If we were clear as to the form of the curve, we should be able to state the height at which it must be drawn above the axis of abscissæ. The mean pressure for the theoretical and for the experimental isothermal must, as before, be the same. Let us consider a simple body which has the same values of a and b as a given homogeneous mixture. Then the experimental isothermal will be a straight line with the same peculiarity as the corresponding line of the mixture. If the mixture is not homogeneous, then the curve must cut the right-hand part of the isothermal lower, and the left-hand part higher, than the corresponding straight line for a homogeneous substance *.

Hence follow various peculiarities of the reduced border-curve for a mixture, as compared with the normal curve. The right-hand side has much similarity to the normal curve; but, for equal values of m, ϵ is smaller for the normal curve. This is especially the case near the highest point, but is less remarkable further away. At the critical point, which is

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* According to these considerations the critical point requires to be defined in a much more complicated way for mixtures than was necessary for simple bodies. It is the point at which the empirical isothermal in the neighbourhood of the critical temperature has three consecutive points in common with the critical isothermal. Hence it may be seen that we are not quite so certain of the critical data which we previously calculated for air.

the end of the normal curve, the two curves will have a common point; but from that onwards the deviation consists in the reduced border-curve sinking less rapidly than the normal curve.

Indeed, in the particular cases mentioned above, there is even a considerable elevation. The discussion of the question whether or not this elevation always persists with diminishing temperatures is very important. Probably it is an elevation which disappears, and at a fixed temperature the pressure at which homogeneity recurs is a maximum. This corresponds better with the idea of a deviation from the form of the normal curve; but an experimental proof of the existence of a maximum pressure has not hitherto been obtained, perhaps because, in the examples given above, a very low temperature must always be required. For this reason I exposed a known mixture of water and ether to high pressures, so as to have a mixture with a higher critical temperature, the ordinary temperature appearing in this case as a low reduced temperature. But though the meniscus in the boundary-surface vanishes, and is replaced by a complete plane, yet at 300 atmospheres a boundary between the two liquids is still clearly visible. It seemed to me, however, to follow from the experiment that, for a mixture of water and ether, ordinary temperatures lie on the descending branch of the curve. With somewhat rapid heating the water becomes turbid, and the turbidity disappears on increasing the pressure. The turbidity is evidently caused by the precipitation of the ether. Consequently a restoration of homogeneity seems to require higher pressures when the temperatures are higher. We have another example of this in the phenomena studied under the title of "Solution of Gases."

Thus also in mixtures a border-curve can be drawn which, at first (for volumes less than the critical volume) lies high above the axis of abscissæ, but which approaches that axis when the temperature is very low, and ultimately reaches it. Hence follows the proposition, "All liquids can mix with one another when the pressure exceeds a certain value."

For the experimental proof of this proposition, very high pressures and very low temperatures must often be used.

Obviously in many cases the transition to the solid state may occur and disturb the experiment. On the other hand, mixtures must be sought, for which the requisite pressure is not altogether too high at ordinary temperatures ; in other words, we must look for a combination of those substances which tend to form a homogeneous mixture at ordinary pressures.

Mixtures of alcohol, ether, and water seem to me to satisfy the above conditions ; but hitherto I have not been able to investigate them. Thus, if ether be poured into alcohol, and then water be added, the mixture is at first homogeneous, but divides into two layers as the quantity of water increases. At the limit a few drops of water poured into the mixture cause a great quantity of ether to separate ; but homogeneity is again restored by a drop of alcohol.

The following numbers prove the property stated above—that for given values of m a smaller value of ϵ is found for that branch of the curve which represents the beginning of the condensation, especially in the neighbourhood of the highest point. The numbers express the results for a mixture of 7 volumes of carbonic acid and 3 volumes of hydrochloric acid. ($t_1=31^\circ{\cdot}6$, $p_1=90$.)

t.	p.	ϵ.	m.
31°	82	0·91	0·998
27	75	0·83	0·985
23·6	69	0·77	0·975
19	63·5	0·70	0·956
16·2	58·5	0·65	0·949
13·2	54·5	0·60	0·939
10·6	51·5	0·57	0·931
8·5	48	0·53	0·924
0	39	0·43	0·897

Comparing these numbers with those given above (p. 460), we see that ϵ is really less at first. When, however, ϵ reaches the value 0·6, there is again such an agreement that the differences are henceforward insignificant.

Although, in general, I ascribe little value to empirical formulæ, yet I have in this case endeavoured to construct an empirical formula for the relation $\epsilon = \phi(m)$, with the view of being better able to compare the laws enunciated with observation. This formula is

$$-\log \epsilon = f \frac{1-m}{m},$$

where f is constant. I have calculated the values of f from the observations of Regnault and Sajotschewsky, as in the following table. Here p_1 is taken $=36{\cdot}9$, and $T_1 = 463°$, and these are supposed to be accurately determined. The values marked with an asterisk have been calculated from the data of Sajotschewsky; the rest from those of Regnault.

t.	*f.*	*t.*	*f.*	*t.*	*f.*
−20°	3·154	50	3·10	120	3·15
−10	3·147	60	3·10	130	3·13 *
0	3·14	70	3·10	140	3·11 *
10	3·13	80	3·10	150	3·13 *
20	3·12	90	3·11	160	3·14 *
30	3·13	100	3·12	170	3·08 *
40	3·11	110	3·13	180	2·84 *

It is only the last value that shows any considerable discrepancy. It is to be observed, however, that an inaccuracy in the determination of T_1 has a great effect in the neighbourhood of this temperature. At 180° it is only necessary to replace $p=31{\cdot}9$ by 31·5, in order to regain the constant 3·1.

Putting for ϵ and m their values $\frac{p}{p_1}$ and $\frac{T}{T_1}$ respectively, the general equation becomes

$$-\log \frac{p}{p_1} = f \frac{T_1 - T}{T},$$

for bodies which are not subject to special conditions, such as dissociation &c.

For all bodies f must have the same value. I will endeavour to show how far observation confirms this, by calculating f indirectly. From the last equation we get

$$\frac{dp}{dT} = f\frac{pT_1}{T^2}\log_\epsilon 10\,;$$

and since

$$\frac{dp}{dt} = \frac{r}{ATu},$$

we get

$$\frac{Apu}{r} = \frac{1}{f\log_\epsilon 10}\cdot\frac{T}{T_1}.^*$$

Now Zeuner has given in his tables the values of $\frac{Apu}{r}$ for several bodies. Supposing these values correct, then we have an equation to find f. For ether-vapour I have almost everywhere found somewhat greater values, as above; but the disagreement is small. Applied to other bodies, we find :—

Water. ($T_1=663$.)		Chloroform.		Acetone.		Carbonic Acid.	
0°	$f=3{\cdot}4$	0°	3·3	0°	3·8	0°	2·9
110	3·1	160	2·7	140	3·0		
209	3·0						

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* This equation shows that the ratio of the external work to the latent heat in vapours depends only on the fraction which the absolute temperature is of the absolute critical temperature. This ratio has its maximum value at the critical temperature, and is then about $\frac{1}{7}$. At this temperature r and u are zero: but the ratio has a fixed value, which is the same for all bodies. Since we have

$$\frac{r}{Apu} = \frac{T}{p}\frac{dp}{dT},$$

it follows that at the critical temperature $\frac{dp}{dT}$ is not equal to zero, as might easily be thought. Supposing the curve of the saturated vapour drawn on the thermodynamic surface, then $p=\phi(T)$ is the projection of this curve on the (p, T) plane. This projection has therefore an extraneous branch.

In addition to this the constants of the empirical formula of Magnus for steam, and of Sajotschewsky for vapour of ether, may serve to confirm the statement that f is at least approximately the same for all bodies. These formulæ are expressed thus—

$$\log \frac{p}{p_0} = \frac{ct}{q+t};$$

and it may be easily deduced that c must be very nearly equal to $\frac{fT_1}{273}$. According to Magnus, c for steam$=7{\cdot}4475$; and according to Sajotschewsky, c for vapour of ether$=5{\cdot}1964$. Hence

$$f = \frac{273}{663} \times 7{\cdot}4475 = 3{\cdot}06 \quad \text{for steam,}$$

and

$$f = \frac{273}{463} \times 5{\cdot}1964 = 3{\cdot}065 \text{ for vapour of ether.}$$

For benzene I find, from the observations of Sajotschewsky, $f=2{\cdot}94$.

The following table contains the values of p calculated from the equation

$$-\log \frac{p}{49{\cdot}5} = 2{\cdot}94 \frac{280{\cdot}6-t}{T},$$

for the data of Sajotschewsky. The calculated pressures stand under p, the observed pressures under p_2, and the differences of the two under A.

t.	p.	p_2.	A.
270°	43·37	43·30	+0·07
260	38·28	38·25	+0·03
250	33·35	33·65	−0·30
240	28·92	29·12	−0·20
230	25·06	24·98	+0·08
220	21·54	21·35	+0·19
210	18·43	18·10	+0·33
200	15·62	15·34	+0·28
190	13·16	13·04	+0·12
180	11·01	11·02	−0·01
80	0·953	1	−0·047

For sulphurous acid we get $f=2\cdot98$ from the pressure at 50°, and $f=3\cdot04$ according to observations at 100°.

For monochlorethane we get $f=2\cdot92$, from the boiling-point (13°·5)[*].

For chloroform $f=2\cdot91$, the boiling-point being 60°.

My purpose was not merely to give these empirical formulæ, but to show in a different manner that the propositions given above are rigorously, or almost rigorously accurate for a number of bodies. If deviations from the rule occur, as in the case of carbon bisulphide and other substances, then the object of investigation will become "an inquiry into the causes why some bodies deviate from the laws laid down."

One cause may perhaps be found in the supposition, which is certainly general, that in liquids a certain number of molecules, at least for a time, are decomposed. This fact, however, belongs to the province of dissociation. Clausius is inclined to this supposition, and, prompted by it, he has introduced the alteration in the form of the isothermal which was mentioned above. But even then, as has been already pointed out, the propositions stated retain their strict validity. Now Clausius has not shown why the decomposition of the molecules, supposing it to occur, should bring about the alteration in question. It would therefore always be possible to ascribe the occasional anomalies to the fact that the molecules of the body are not perfectly equal to each other. But such a body, in which several molecules have united, must be regarded as a mixture. The laws for mixtures have shown that the pressure is a function of the volume. But since this property has not been observed in bodies such as carbon bisulphide, the hypothesis that the anomalies arise from the temporary decomposition of the molecules loses much of its probability. It seems to me, rather, that the cause is to be sought in a variation of the size of the molecule[†].

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[*] The boiling-point is nearer 12°·1.

[†] [Since this was set up we have received a copy of a new paper by Prof. J. D. Van der Waals (*Extrait des Archives Néerlandaises*, t. xxiv. pp. 1–56), entitled "*Théorie Moléculaire d'une substance composée de deux matières différentes,*" in which the conditions of stability of mixtures are treated at considerable length by the method of Gibbs.—*Note by the English Translators.*]

CHAPTER XIII.

The Coefficients of Expansion and Compressibility in Corresponding States of different Liquids.

[*Note.*—This chapter does not appear as part of the original essay, but is due partly or wholly to Dr. Roth.]

FROM the foregoing considerations some conclusions may be drawn as to the values of the coefficients of expansion and compressibility for different bodies, especially in the liquid state. For better illustration I premise some remarks. Consider three mutually rectangular axes—volume, pressure, and temperature; then we get a thermodynamic surface, which must be the same for all bodies. It is only when the three coordinates are expressed in terms of the usual units that there will be a different surface for each body. These surfaces constitute a group, or in geometrical language a family; and the properties of such a group may be used to establish relations for the various properties of bodies which depend on *v*, *p*, and T. To every point on the one surface belongs a corresponding point on a second surface; and by this means continually corresponding states of the two bodies may be determined.

Thus a section perpendicular to the *p*-axis gives a relation between *v* and T for the pressure *p*; and if a similarly situated plane is drawn at a corresponding distance, to cut the surface representing the state of the second body, we have a relation between *v* and T for the two bodies under corresponding pressures. To a pair of infinitely close points in the first section corresponds a pair of infinitely close points in the second section. Accordingly it is easy to find the relation which must exist between the values of $\frac{1}{v}$ (limit $\frac{\Delta v}{\Delta t}$) for two bodies in such corresponding states. This quantity is the coefficient of expansion at given T and under given *p*. Now, when $\frac{\Delta v}{v}$ is the same for two bodies, the values of the above coefficient of expansion must be inversely proportional to the values of ΔT, if the two bodies always remain in corresponding states. Therefore:—

"The coefficients of expansion of bodies in corresponding states are inversely proportional to the absolute critical temperatures."

This may be shown algebraically as follows:—If p_1 is the critical pressure, v_1 the critical volume, and T_1 the critical temperature, and, as before

$$p = \epsilon p_1, \quad v = nv_1, \quad T = mT_1\,;$$

then (pp. 455 *et seq.*)

$$n = \phi(\epsilon, m)$$

or

$$\frac{v}{v_1} = \phi\left(\frac{T}{T_1}, \frac{p}{p_1}\right).$$

The function ϕ is the same for all bodies, as appeared above. Differentiating with respect to T, regarding p as constant, we get

$$\frac{1}{v_1}\frac{dv}{dT} = \phi' . \frac{1}{T_1}\,;$$

and therefore

$$\frac{1}{v}\frac{dv}{dT} = \frac{\phi'}{\phi} . \frac{1}{T_1}.$$

If, instead of $\frac{1}{v}$(limit $\frac{\Delta v}{\Delta T}$) we consider $\frac{1}{v}\frac{\Delta v}{\Delta T}$ itself (which is the mean coefficient of expansion at pressure p when the temperature increases from T to $T + \Delta T$), then this mean coefficient must also be inversely proportional to T_1, provided the heating of both bodies is so regulated that they are always in corresponding states.

The expression $\frac{\Delta v}{v}$ will be the same for all bodies if they are heated under corresponding pressures through a number of degrees proportional to T_1, provided the heating begins at a temperature proportional to T_1.

By drawing plane sections perpendicular to the T-axis, we get, in a similar manner, the following propositions:—Denoting by $-\frac{1}{v}\frac{dv}{dp}$ the coefficient of compressibility β, then "At corresponding temperatures and pressures the coefficients of compressibility are inversely proportional to the critical pressure." And similarly the mean coefficient is inversely proportional to the critical pressure.

These relations follow from the equation given for the isothermal in accordance with the former considerations; but the proof is confined to volumes $> 2b$. They are, however, as I have shown above, valid to a high degree of approximation when small volumes are considered, and therefore I have extended them to a much greater part of the isothermal. In doing so, Kopp's law for the determination of the volume of the molecules may, among others, be applied to the verification. At the same time there will be found a property of the function of the molecular volume denoted by b in those cases where the volume is less than $2b$. This property is that b (which denotes four times the volume of the molecules when the whole volume is greater than eight times the volume of the molecules) will be always the same multiple of this volume for bodies in corresponding states.

Accurate determinations for a verification of the proposition concerning the coefficients of expansion are available from the researches, among others, of Kopp and of Pierre. These observations, however, were not made at corresponding pressures, since the pressure of one atmosphere does not give the same value of ϵ for every substance. The coefficient of expansion, however, depends very little on the pressure at pressures which are only a small fraction of the critical pressure. The observers mentioned have embodied their results in empirical formulæ, expressing the volume from 0° up to the boiling-point, thus

$$v_t = v_0(1 + at + bt^2 + ct^3).$$

For our purpose the following calculations are to be made:—First, let a set of corresponding temperatures t', t'', t''', ... be found from

$$\frac{273 + t'}{T_1} = \frac{273 + t''}{T_2} = \frac{273 + t'''}{T_3} = \text{\&c.}$$

These are to be substituted in $\frac{1}{v}\frac{dv}{dT}$, and then the expression

$$\frac{a + 2bt + 3ct^2}{1 + at + bt^2 + ct} T_1$$

must have the same value for all bodies. It must be borne in mind, however, that the set of temperatures must lie within the limits for which the empirical formula holds.

The following is perhaps the most accurate investigation as to whether the coefficients of expansion of substances in corresponding states agree with our proposition. When the empirical formula for one substance is given, then the empirical formula for every other substance whose critical point is known can be calculated. The formula thus obtained can then be compared with that derived from the observations. Thus, from the particular formulæ of Pierre for bodies whose critical temperatures are determined, I have calculated the formula for ether. Assuming, then, that the observations are completely unobjectionable, and are accurately represented by the empirical formula, we must get the separately calculated formulæ to agree not only with each other but also with the empirical formula of the observer.

Making a calculation with this object, the process is as follows :—For example, to find the formula for ether from that for chloroform. From the equation

$$\frac{273}{463} = \frac{273+\theta}{533},$$

we get the temperature for chloroform which corresponds to 0° for ether (463° and 533° are the absolute critical temperatures for ether and chloroform). Let the formula for chloroform be

$$v_t = v_0(1 + at + bt^2 + ct^3).$$

Then calculate

$$a' = \frac{533}{463} \cdot \frac{a + 2b\theta + 3c\theta^2}{1 + a\theta + b\theta^2 + c\theta^3},$$

$$b' = \left(\frac{533}{463}\right)^2 \cdot \frac{b + 3c\theta}{1 + a\theta + b\theta^2 + c\ {}^3},$$

$$c' = \left(\frac{533}{463}\right)^3 \cdot \frac{c}{1 + a\theta + b\theta^2 + c\theta^3}.$$

Then the calculated formula for ether will be

$$V_t = V_0(1 + a't + b't^2 + c't^3).$$

This is easily seen ; but it is abundantly proved as follows :—

Writing

$$v_t = v_0(1+at+bt^2+ct^3)$$
$$= v_0(1+a(\theta+t')+b(\theta+t')^2+c(\theta+t')^3),$$

then

$$v_{t'} = v_0\{(1+a\theta+b\theta^2+c\theta^3)+(a+2b\theta+3c\theta^2)t' + (b+3c\theta)t'^2+ct'^3\}$$

expresses the volume of the chloroform, where t' is reckoned from θ and not from 0. The last equation may be put in the form

$$v_{t'} = v_\theta\left\{1+\frac{a+2b\theta+3c\theta^2}{1+a\theta+b\theta^2+c\theta^3}t'+\frac{b+3c\theta}{1+a\theta+b\theta^2+c\theta^3}t'^2 + \frac{c}{1+a\theta+b\theta^2+c\theta^3}t'^3\right\}.$$

If the pressures of two substances correspond, or if they may without much error be considered to correspond, then V_0 (for ether) and v_θ (for chloroform) must be corresponding volumes; and also V_t (the volume of the ether after being heated through t°) and $v_{t'}$ (the volume of the chloroform after being heated through t' above θ) will be corresponding volumes, provided $\frac{t}{463}=\frac{t'}{533}$. Hence it follows that $\frac{V_t}{V_0}=\frac{v_{t'}}{v_\theta}$ for every value of t which makes $t'=\frac{533}{463}t$; and hence the values of a', b', c' are as stated above.

The observations of Pierre (*Ann. de Chim. et de Phys.* [3] xv., xix., xxi., xxxiii.) extend to a great number of bodies, but the critical temperatures of most of these are unknown. In the case of alcohol, bisulphide of carbon, ether, monochlorethane, ethylic formate, ethylic acetate, sulphurous acid, and chloroform, these critical temperatures have been carefully determined by Sajotschewsky. I have excluded alcohol for the same reasons as before. For the remaining bodies I have made the calculations indicated above. The following table, after the name of the body, gives the formula for ether as calculated from that of the body named. Each of the coefficients is to be multiplied by 10^{-7}.

Carbon bisulphide .	$1+15600t+55t^2+0{\cdot}29t^3$.
Monochlorethane .	$1+15360t+25t^2+0{\cdot}15t^3$.

Chloroform . . . $1+15340t+32t^2+0{\cdot}25t^3$.
Ethyl formate . . $1+15470t+38t^2+0{\cdot}08t^3$.
Methyl acetate . . $1+15140t+17t^2+0{\cdot}05t^3$.
Ethyl acetate . . $1+15300t+37t^2+0{\cdot}02t^3$.

Pierre gives

Ether . . . . . . $1+15130t+23{\cdot}6t^2+0{\cdot}40t^3$.

This result exhibits a remarkable confirmation of the proposition, even supposing the observations and the empirical formulæ resulting from them to be quite reliable. It happens in this case that the calculated formulæ all give a somewhat greater expansion than was observed. This is not so in the case of other bodies (*cf.* p. 493).

From the calculated formulæ it follows, first, that at temperatures corresponding to 0° for ether, the products of the coefficient of expansion into the absolute critical temperature are proportional to the numbers

1560, 1536, 1534, 1547, 1514, 1530, 1513.

Sulphurous acid, however, gives the number 1610, according to the observations of Pierre; and thus there is here a considerable departure from the rule. This is the more remarkable as sulphurous acid regularly follows the law for the vapour-pressure, even at temperatures for which Pierre investigated the expansion. Thus the formula

$$-\log\frac{p}{p_1}=f\,.\,\frac{1-m}{m}$$

requires (at the boiling-point, -8°) the value $3{\cdot}06$ for f, as in the case of ether. Pierre, indeed, observed sulphurous acid within an interval of only 16° to 38°; and for fixing the three coefficients a, b, c, only three observations can properly be used. In addition to this even he himself speaks of the given formula with some doubt, and considers the observations less accurate than those for the other bodies. Thus it may perhaps be admitted that the expansion of sulphurous acid is not yet sufficiently accurately known.

The observations of Kopp on ether, ethyl formate, ethyl acetate, benzene, methyl acetate, and acetone may be considered. The formulæ given in the following table are calculated for monochlorethane, in the same way as above, from the empirical formulæ of the substances mentioned. The coefficients are to be multiplied by 10^{-7}.

Ether	$1+15240t+39{\cdot}56t^2+0{\cdot}28t^3$.
Ethyl formate .	$1+15580t+25{\cdot}54t^2+0{\cdot}47t^3$.
Ethyl acetate . .	$1+15770t+41{\cdot}26t^2+0{\cdot}16t^3$.
Benzene . . .	$1+15940t+37{\cdot}13t^2+0{\cdot}13t^3$.
Methyl acetate .	$1+16050t+45{\cdot}83t^2+0{\cdot}04t^3$.
Acetone . . .	$1+16340t+43{\cdot}10t^2+0{\cdot}15t^3$.

Kopp himself gives no observations for monochlorethane. According to Pierre we have

Monochlorethane . $1+15750t+28{\cdot}13t^2+0{\cdot}16t^3$.

The agreement here is not so good as before. Yet the observations of Pierre and Kopp, though in many respects agreeing excellently, show discrepancies here and there; so that the question how far the validity of our proposition extends cannot be decided by them. While an observer such as Kopp finds the values 0·00144 and 0·00151 for the coefficient of expansion of the same body (ether at 0°), the discrepancies of the values observed experimentally are not less than those of the calculated values.

Water also may be adduced as a test, although its critical temperature is not accurately known (410° according to Cagniard de la Tour's estimate, 390° according to earlier observations; *cf.* p. 463). Hirn has investigated the expansion of water between 15 and 200 atmospheres' pressure. Taking 410° as the critical temperature of water, then 128° for water corresponds to 0° for ether; and the expansion per unit volume for ether from 0° to 10° must be equal to that for water from 128° * to 142°·75. To a rise of 10° for ether corresponds a rise of 14°·75 for water. According to the experiments of Pierre and Hirn—

Ether.		Water.	
0°–10° . .	0·01541	128° –142°·75 .	0·01407
10 –20 . .	0·01613	142·75–157 ·5 .	0·01520
20 –30 . .	0·01707	157·5 –172 ·25 .	0·01736

Although these values do not agree, yet the mean value for ether between 0° and 35° corresponds to that for water between 128° and 180° to a degree sufficient to confirm our proposition. With 390° as the critical temperature of water, all the numbers for that substance would turn out a little less than those given above.

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* [We make this 129°·7 instead of 128°.—*Note by the English Translators.*]

We have no data to test the law for the coefficients of compressibility (see below). We have indeed observations for three bodies whose critical temperatures are known; but they are not observations at corresponding temperatures and pressures, and it has been sufficiently shown that the coefficient of compressibility depends very much on the temperature.

The critical pressure of chloroform is about $\frac{3}{2}$ times greater than that of ether; and therefore, according to our rule, the coefficient of compressibility for the first of these substances would be two thirds that for the second. Now β_0 for ether is 0·000111, so that β_{41} for chloroform must be 0·000074. Grassi gives for chloroform $\beta_{8\cdot5}=0\cdot000625$ and $\beta_{12\cdot5}=0\cdot0000648$.

The critical pressure of carbon bisulphide is twice that of ether, and thus β_{48} for carbon bisulphide must be half of β_0 for ether, or 0·000056. Amaury and Descamps give 0·000063 for this body.

Prof. E. Wiedemann called my* attention lately to Amagat's investigations on the compressibility of liquids†. Although I must attribute to Amagat's results great significance in the extension of our knowledge of the coefficient of compressibility, and even of the variability of this coefficient with increasing temperature, yet, on comparing them with the results of other observers, the discrepancy is usually so great that their accuracy cannot be regarded as raised above all doubt. Thus, Amagat finds for ether at 13°·7 the value $\beta=0\cdot000167$, independently of the limits of pressure; Grassi gives $\beta_{14}=0\cdot000140$ and $\beta_{13\cdot8}=0\cdot000153$, the increment of pressure being respectively 1·58 and 8·4 atmospheres. Similarly for alcohol:

Amagat	β_{14}	$=0\cdot000101$.
Grassi	$\beta_{13\cdot1}$	$=0\cdot000090$.
	,,	$=0\cdot000099$.

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* [*I. e.* Dr. Roth's.]

† *Ann. de Chim. et de Phys.* xi. pp. 520–549, 1877; *Beibl.* i. p. 489, 1877: the treatment of Amagat's investigations is added supplementarily.

For carbon bisulphide:

Amagat . . . . . . $\beta_{15\cdot6}=0\cdot000087$.
Amaury and Descamps. $\beta_{14}=0\cdot000063$.

Where there are values given by other observers available for comparison, Amagat always gives the greatest value.

On the other hand, from a fresh investigation by Ramsay (Proc. Roy. Soc. Lond. xxxi. pp. 194–206, 1881) the differences which may be found for the critical point of the same substance become very striking. Thus for ether there is found by

Ramsay . . . $t_1=195^\circ\cdot5$, $p_1=40$.
Sajotschewsky . $t_1=190^\circ$, $p_1=36\cdot9$.

Again, for benzene,

Ramsay . . . $t_1=291^\circ\cdot7$, $p_1=60\cdot5$.
Sajotschewsky . $t_1=280^\circ\cdot6$, $p_1=49\cdot5$.

Probably these discrepancies are due to impurities, which are imperceptible at ordinary temperatures. They have not much weight against the law given above for the vapour pressure, since the greater pressure corresponds in some measure to the increased temperature. Thus Ramsay gives, as the maximum pressure of ether at 190°, nearly the same value which Sajotschewsky finds for the critical pressure. If, however, we endeavour to use these observations as a test of other laws, the discrepancies mentioned will become very sensible.

Consequently it may be considered rash to endeavour to pronounce a decisive judgment on the validity of the law for the coefficient of compressibility. Yet perhaps it ought not to be said that Amagat's results contradict this law. By taking Ramsay's values as data for the critical point of ether instead of Amagat's, almost all the observations agree well with the law, as appears from the following table. Opposite to Amagat's numbers for ether are given those which have been calculated by means of our law for his observations on the compressibility of other substances. The values for the critical points of the other liquids are taken from Sajotschewsky's observations.

t.	Ether.	$10^6 \beta$, calculated from the observations on					
		Mono-chlorethane.	Alcohol.	Methyl acetate.	Acetone.	Chloro-form.	Benzene.
13°·5	167						
17	......	182					
22·7	......	194					
25·4	190						
42·5	......	......	......	......	......	......	215
54·5	......	......	......	......	......	282	
63	300						
71	......	337	323				
72	......	......	......	......	358		
74	......	......	.....	370			
78·5	367						
90·1	......	474					
99	555						
100	......	672					

If we had used carbon bisulphide and ethyl acetate we should have found discrepancies.

For monochlorethane Amagat finds a formula of Duprée confirmed. The formula in question coincides with

$$T\left(\frac{dp}{dT}\right)_v = \frac{a}{v^2},$$

which is derived from our fundamental equation if we neglect the external pressure in comparison with the molecular pressure, a course which we have considered to be allowable for liquids.

I have hitherto investigated the changes which the volume in corresponding states undergoes in consequence of changes in p and t. It remains still to discuss how far the value of v for all bodies may be exhibited as the same fraction of the critical volume.

Our theory gives the critical volume as the product of $3b$ into the volume at 0° and under 760 mm. pressure ; b is equal to $4b_1$, and b_1 is the volume of the molecules. Consequently

$\frac{b}{4}$ of the volume of gas at 0° and 760 mm. will denote the space really occupied by the molecules. Now our theory requires that the volume of all substances taken in corresponding states shall be the same multiple of the volume of the molecules reckoned as above. Thus, for example, the volume of one kilogram of gaseous ether at 0° and 760 mm. is 302 litres; and hence tne volume of the molecules is 0·4341 litre, as appears by using the value of $b=0{\cdot}00575$, derived from Sajotschewsky's observations. The apparent liquid volume at 0° and 760 mm. is 1·396 litres, if the density is taken to be 0·716 (though this is sometimes taken 0·715, and even 0·736); thus the liquid volume is 3·25 times the volume really occupied by the molecules. The following table gives the value of this factor for other bodies, where it is to be remarked that the apparent volume must be taken for corresponding values of p and t:—

Ether	3·25	Chloroform . .	3·35
Water	3·26	Monochlorethane .	3·15
Carbon bisulphide .	3·42	Ethyl acetate . .	3·28
Benzene	3·25	Ethyl formate . .	3·10
Acetone	3·46	Sulphurous acid .	3·11

For the calculation of these numbers there is required a knowledge of the critical temperature, the critical pressure, the molecular weight, the density at 0°, the coefficient of expansion, and, strictly speaking, the coefficient of compressibility as well; and therefore the agreement may be regarded as very satisfactory.

Moreover, it must be remembered that the theory supposes the molecules to remain individually separate, even at the highest degree of condensation, and further that on the whole there is no combination of the molecules so as to form more complex groups. This is by no means certain *à priori*, and was indeed only assumed to simplify the treatment; in order to bring the matter to a satisfactory conclusion, the treatment must be freed from this assumption and the results compared with experiment.

The agreement hitherto obtained, however, is sufficiently good to warrant us in saying that complex groupings can only exist to a limited extent, if at all. Dissociation shows that something depends on the nature of the substances employed.

If the factor last investigated has always the same value, then a simple rule may be deduced for calculating the density of a liquid at a temperature corresponding to 0° for ether, provided the data of the critical point are known. If, however, the factor has different values, then the density in any case can be only approximately found. The value of the factor being taken as 3·25, the density of diethylamine ($p_1=38{\cdot}7$, $T_1=493°$) comes to be about the same as that of ether.

At first I had no experimental data for the density of diethylamine; but Prof. A. C. Oudemans was good enough to determine it and place the results at my disposal (Supplementary addition from *Natuurk. Verh. der Koningkl. Akad.* Deel xi. p. 10, 1881).

From the general law for liquids, it follows that in corresponding states $\frac{v}{v_1}$ has the same value for all bodies, where v_1 denotes the critical volume. Now consider a new corresponding state for the unit of weight of different bodies, so that

$$v = nv_1, \quad p = \epsilon p_1, \quad T = mT_1,$$

where, in the equation

$$\frac{vp}{T} = \frac{n\epsilon}{m}\frac{v_1 p_1}{T_1}$$

the values of n, ϵ, and m are the same for all bodies; then, for a sufficiently great value of v, each side of the last equation will be inversely proportional to the molecular weight. Hence it follows that

$$\frac{1}{v_1} = \frac{n\epsilon}{m}\frac{\mu_1 p_1}{T_1}.$$

If d_1 and d_2 denote the densities of two bodies in corresponding states, the last equation gives

$$\frac{d_1}{d_2} = \frac{\mu_1 p_1 T_2}{\mu_2 p_2 T_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The method adopted in establishing the above equation indicates that it may hold even in those cases where Avogadro's law becomes open to question, viz. in cases of abnormal vapour-density. It appears further that, within limits which are not extremely wide, the given relation enables a judgment to be formed as to normal or abnormal liquid-density.

Now applying formula (1) to the comparison of the densities of ether and diethylamine, since for ether

$$\mu_2 = 74, \quad p_2 = 36{\cdot}9, \quad T_2 = 463°,$$

and for diethylamine

$$\mu_1 = 73, \quad p_1 = 38{\cdot}7, \quad T_1 = 493°,$$

we have

$$\frac{d_1}{d_2} = 0{\cdot}972.$$

If d_2 is the density of ether at 0° and under the pressure of one atmosphere, then d_1 is the density of diethylamine at 17°·7 and under a pressure of 1·05 atmospheres. Prof. Oudemans found that the density of diethylamine at 18° and 1 atmosphere was 0·70847. With the value given by Kopp for ether, 0·736, we shall have

$$\frac{d_1}{d_2} = 0{\cdot}963.$$

The discrepancy is only about 1 per cent., and is fully accounted for by the errors in the determination of the critical point.

The law of the coefficient of expansion may also be tested by means of Oudemans' investigation. After the preceding results had been communicated to me, I calculated the empirical formula, in the manner given above (p. 482), from that given by Pierre for ether. If the formula for diethylamine is to be thus calculated for temperatures from 0° to t°, it must be assumed that Pierre's formula for ether remains valid some degrees below zero. Though there is probably little doubt about this, it may be taken with reservation. Thus, for the volume of the diethylamine, expressed in terms of its volume at 0°, we get the equation

$$V_t = V_0(1 + 0{\cdot}001413t + 0{\cdot}00000035t^2 + 0{\cdot}000000034t^3).$$

Prof. Oudemans made two sets of observations on a purified preparation of diethylamine obtained by distilling only 25 c. cm. from a volume of 70 c. cm. One set of observations was made with a Geissler's pyknometer capable of holding 22 c. cm. and having a thermometer ground in ; the other set of observations with a Gay-Lussac's bottle holding 10 c. cm. The result of each series was that the diethylamine expands uniformly.

According to the first set (0° to 40°),

$$V_t = V_0(1+0{\cdot}0015165t)\ldots(d_0=0{\cdot}72776);$$

according to the second set (0° to 54°),

$$V_t = V_0(1+0{\cdot}001554t)\ldots(d_0=0{\cdot}72809).$$

The diethylamine used in the experiment appeared, however, on closer investigation, to be not quite homogeneous ; so it was separated by distillation into two portions, the first consisting of 14, the last of 11 c. c. The first portion had a density 0·72723 at 0°, the second portion the density 0·72906. On account of the constancy of its boiling-point, amongst other reasons, the first part seemed the most trustworthy, and was again investigated in the Gay-Lussac's bottle. Repeated weighings at 0°, 18°, 36°, 54° gave the specific gravity

$$d_0=0{\cdot}72723,\quad d_{18}=0{\cdot}70840,\quad d_{36}=0{\cdot}69829,\quad d_{54}=0{\cdot}66990.$$

Hence Prof. Oudemans derives

$$V_t=V_0(1+0{\cdot}0014117t+0{\cdot}000003349t^2-0{\cdot}0000000026t^3).$$

Although the coefficients of t^2 and of t^3 differ considerably, yet, for the coefficient of t the agreement is such that we may perceive in it quite a definite confirmation of the general law.

SUPPLEMENT TO THE NINTH AND TENTH CHAPTERS.

BY DR. ROTH.

Further Values of K. (*Cf.* reference, p. 491).

AN attempt has already been made in the Ninth Chapter to find definite values for the molecular pressure in liquids, the quantity K, in fact, which appears in Laplace's theory of capillarity.

According to the general law, this quantity, for corresponding states of different liquids, must be proportional to the critical pressure. The numerical values which I found for ether, alcohol, and carbon bisulphide agree fairly well with this law. But the values for water are aberrant.

The following table gives a set of values, calculated according to the above law, for bodies in states corresponding to the state of ether at 0° and under the pressure of 1 atmosphere :—

	atmosph.		atmosph.
Ether	1430	Methylic acetate .	2225
Alcohol	2400	Water	10700
Carbon bisulphide	2890	Monochlorethane .	2040
Sulphurous acid .	3060	Diethylamine . .	1500
Carbonic acid . .	2820		

The quantity K does not lend itself to experimental determination. The calculated values, however, are important, as helping us to answer a question of great importance to the theory of capillarity, namely, whether the radius of the so-called sphere of action is the same for all bodies, or not; and whether the values of it are or are not connected with the dimensions of the molecules.

The answer, which might be given *à priori* to this, depends on the conception formed of forces in general and of cohesion in particular. Regarding the matter from Newton's point of view (so-called), and considering the molecular forces as "acting at a distance," then the radius of the sphere of action may indeed be regarded as having the same value for all bodies. But if we start by considering molecular forces as sensible only when the molecules are in contact, then we must attribute different values to the radius of the sphere of action, and let it embrace an equal number of molecular layers.

The conclusion has already been arrived at (p. 438) that the ratio of the capillarity-constant to the molecular pressure (which is directly connected with the radius of the sphere of action) is equal to the diameter of the molecules ; so that we must take into account equally great fractions of a single layer instead of an equal number of layers. For, in the corresponding states of different bodies the distance between the different layers is proportional to the dimensions of the molecules.

In other words, if the radius of attraction has the same value for all bodies, then the capillarity-constant for different bodies must be proportional to the critical pressure. If, on the other hand, that radius is proportional to the linear dimensions of the molecules, we arrive at the following relation:—

$$\left(\frac{H_1}{H_2}\right)^3 = \frac{p_1{}^2\,T_1}{p_2{}^2\,T_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here p and T denote the critical pressure and critical temperature of a body, and H is the capillarity-constant. This of course only refers to liquids in corresponding states, and strictly speaking to such as are bounded as to their surface by their own vapour only.

In the following table, if we put the capillarity-constant for ether $=1$, then equation (2) gives the values of the constants in column I.; under II. are the observed values, and under III. the ratios of the critical pressures.

	I.	II.	III.
Ether	1	1	1
Alcohol	1·46	1·3	1·7
Carbon bisulphide	1·69	1·8	2·05
Water	4·3	4·2	7·5
Ethylic acetate	1·39	1·42	1·56
Acetone	1·3	1·4	1·42
Chloroform	1·37	1·49	1·48

The result for water seems to afford some evidence in favour of equation (2). The results for the other bodies, however, leave it still undecided which of the two hypotheses as to the magnitude of the radius of the sphere of action is to be preferred. With respect to the values under II. it may be remarked that, properly speaking, they are true only for ordinary temperatures, and also that some uncertainty attaches to them, since the different observations show no concordant, results. I myself determined the values for methylic acetate, chloroform, so-called chloral-chloroform, with preparations which I might consider pure. With this object I took two capillary tubes and arranged matters so that the three liquids, ether, chloroform, and methylic acetate, rose to a fixed mark in each tube. Thus the radius of the tubes, and in like manner the greater or less departure from an exactly circular cross section, had not to be specially considered. The ratio of the products of the heights to which the liquids rose into the densities gave the ratio of the capillary constants. In one tube the heights risen to were

For Ether	20 mm.
„ Methylic acetate . .	22 „
„ Chloroform	14·5 „

In the second tube the heights were

For Ether	14 mm.
„ Methylic acetate . .	15·4 „
„ Chloroform	10·1 „

Finally, a remark on the critical temperature of aldehyde. From a comparison of the coefficient of expansion of this body with that of ether and monochlorethane, it appears that the critical temperature of aldehyde lies between those of the two other bodies. Thus the coefficient of expansion at 0° is

For Ether	0·001513
„ Aldehyde	0·001546
„ Monochlorethane . .	0·001575

Ether has the critical temperature 190°, and monochlorethane 182°. Now two different observations gave for aldehyde 182° and 181°. The liquid was introduced into thick glass tubes as free from air as possible, and was then heated. The tube still contained a certain quantity of air, which seemed to have got in during the sealing of the tube. Aldehyde cannot be kept at a high temperature for any length of time, since it soon becomes completely altered. Finally, the aldehyde, originally colourless, had changed into a clear brownish liquid, which, when again heated to 182°, showed no sign of the critical state.

PHYSICAL MEMOIRS. Vol. I.

CORRECTIONS.

[SUPPLIED BY R. E. BAYNES, M.A.]

Page 1,	line	3	from bottom.	*For* or *read* of.
,, 5,	,,	22	,, top.	*For* also *read* therefore.
,, 5,	,,	24	,, ,,	*For* electric *read* molecular.
,, 6.	,,	7	,, ,,	*For* insulated *read* insulating.
,, 6.		...	...	*Add a note*: [The coefficient in line 23 should be $\frac{1}{4}$, not $\frac{1}{2}$.]
,, 7,	,,	2	from bottom.	*For* obviously *read* probably.
,, 9,	,,	1	,, top.	*For* distance from *read* path of.
,, 9,	,,	7	,, ,,	*For* from *read* of.
,, 9,	,,	7	,, ,,	*Transpose* which . . . silk *after* quadrant.
,, 9,	,,	26	,, ,,	*After* tinfoil *add* joined to them.
,, 9,	,,	4	,, bottom.	*Before* cushion *add* back edge of the.
,, 12,	,,	11	,, top.	*For* the influence of the *read* the uniform influence of their.
,, 15,	,,	17	,, ,,	*For* (2*c*) *read* (2*d*).
,, 15,	,,	1	,, bottom.	*For* $\phi_a - \phi$ *read* $\phi_a - \phi_i$.
,, 16,	,,	2	,, top.	*For* $\phi_i - \phi_a$ *read* $\phi - \phi_a$.
,, 16.		...	...	In equation (3 *b*) *for* ϕ *read* ϕ_i.
,, 18,	,,	5	,, bottom.	*For* quantity *read* volume.
,, 18,	,,	5	,, ,,	*Before* to *add* of the solution.
,, 19.		...	...	Strike out the note: for there is no misprint, the calculation being based on the amount of *cu* deposited (see p. 18, l. 6 from top) doubtless in a supplementary electrolytic cell.
,, 24,	,,	15	from top.	*For* σ *read* σ_1.
,, 25.		...	...	*Add a note*: [$(\phi_i - \phi_a)$ should be added as a factor on the right-hand side of the equations in lines 9, 12, 13.]
,, 27,	,,	3	from bottom.	*For* $\frac{J\sigma}{4\pi k^2 \phi}$ *read* $\frac{J\sigma\phi}{4\pi k^2}$.
,, 28,	,,	6	,, ,,	*For* each electric discharge *read* equal electric discharges.
,, 29,	,,	5	,, top.	*For* 6, 9 *read* 6·9.
,, 33,	,,	12	,, ,,	*For* $-\frac{\partial u}{\partial y}$ *read* $-\frac{\partial u}{\partial z}$.
,, 33.		...	...	*Add a note*: [The k^2 of equation (12) etc. is not the same as the k^2 of equation (1), but is ϵ times less.]
,, 34,	,,	20	from top.	*For* σ_1^2 *read* σ^2.

Page 34, line 23 from top.	*For* $-\frac{\sigma^4}{2.2.4.4}+\frac{\sigma^6}{2.2.4.4.6.6}$ *read* $+\frac{\sigma^4}{2.2.4.4}-\frac{\sigma^6}{2.2.4.4.6.6}+$
,, 34, ,, 3 ,, bottom.	*For* 1·1445 *read* 1·1441, which is the number given on p. 18.
,, 35.	*Add a note*: [5·777 in line1 6 should be corrected to 5·269.]
,, 41, ,, 13 ,, top.	*After* efflux *add* without friction.
,, 42, ,, 11 ,, ,,	*For* increasing *read* decreasing.
,, 43, ,, 11 ,, bottom.	*For* last *read* alterations.
,, 45, ,, 1 ,, top.	*Before* be *add* have to.
,, 48, ,, 10 ,, bottom.	*For* during the last year *read* of late years.
,, 49, ,, 5 ,, ,,	*Dele* the negative of which is *and after* Force Function *add* (when negatively taken).
,, 50, ,, 4 ,, top.	*For* definite function of mechanical changes *read* function of definite mechanical changes.
,, 50.	*Add a note*: [In the above quotation $\frac{\partial S}{\partial \theta}$ should be multiplied by $\mathfrak{J}$.]
,, 51, ,, 8 from bottom.	*For* $\int \frac{\partial Q}{\theta} . d\theta$ *read* $\int \frac{dQ}{\theta}$.
52, ,, 3 ,, top.	*For* one of which *read* which function for one parameter.
,, 53, ,, 5 ,, ,,	*For* $\frac{d\mathfrak{F}}{d\theta}$ *read* $\frac{\partial \mathfrak{F}}{\partial \theta}$.
,, 53, ,, 5 ,, bottom.	*For* contant *read* constant.
,, 53.	*Add a note*: [$\partial U/\partial \theta$ in line 6 from bottom should be divided by $\mathfrak{J}$].
,, 57, ,, 2 from bottom.	*For* $d\mathfrak{F}$ *read* $-d\mathfrak{F}$.
,, 68.	*Add a note*: [The last integral in equation (2 *a*) is not correct, for, although the upper limit of the integral is a function of h, the curve along which the integral is taken is independent of h.]
,, 68, 4 from bottom.	*For* (2 *b*) *read* (1 *d*).
,, 68, ,, 3 ,, ,,	*For* (2) *read* (2 *b*).
,, 86, ,, 4 of note.	*For* 3904·8, or nearly *read* 3904·627, or exactly.
,, 87, ,, 6 from top.	*In the first denominator write* $2a_h$ *for* $2a$.
,, 87.	*Add a note*: [The sign of H must be changed in (1 *c*) and in equations (3) and (3 *b*) following.]
,, 89, ,, 10 from bottom.	*For* Πere *read* Here.
,, 91.	*Strike out the whole note* † *and replace it by* [The value of $\mathfrak{f}_a$ should be 0·4279.]
,, 91, ,, 12 from top.	*For* $\mathfrak{f}$ *read* $\mathfrak{f}_a$.
,, 91, ,, 13 ,, ,,	*In the value of* H_a *the sign of* $\mathfrak{J} . \mathfrak{l}_a . \log \theta_o$ *should be* $-$.
,, 92, ,, 7 ,, ,,	*For* b *read* b_o.
,, 92, ,, 8 ,, ,,	*For* (2 *b*) *read* (3 *c*).
,, 107, ,, 8 ,, bottom.	*For* A_o *read* A_a.